

# **Wisconsin Urban Air Toxics Monitoring**

**A Summary Report for the Period  
July 1996 - June 1997**

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# Wisconsin Urban Air Toxics Monitoring

## Executive Summary

The Clean Air Act Amendments of 1990 define an approach to Hazardous Air Pollutants (HAPS) which includes seeking a substantial reduction in emissions and public health risks associated with exposures. As a part of this, a research program is outlined which includes ambient monitoring for a broad range of HAPs in a representative number of urban locations.

The Wisconsin Urban Air Toxics Monitoring Network (WUATM) was conceived in response to these directives. The full network was originally planned to consist of 4 or 5 multi-parameter monitoring stations located throughout the state. A single prototype site was established in Green Bay during 1991. Although funding for additional full sites has yet to be appropriated, a number of additional sites have been established for one or more of the parameter groupings.

The following sites have incorporated some or all of the current WUATM parameter list:

- ◆ Bay Beach, Green Bay (55-009-0023) July 1991 - March 1993 (full site)
- ◆ Fox River, Green Bay (55-009-0021) April 1993 - June 1997 (full site)
- ◆ Winter St., Superior (55-031-0034) July 1996 - present (metals)
- ◆ Melendez Site, Waukesha (55-133-0018) July 1996 - present (metals)
- ◆ Great Lakes Research Center, Milwaukee (55-079-0064) July 1996 - present (metals)
- ◆ Trout Lake Research Station, Boulder Junction (55-125-0001) July 1996 - present (metals)
- ◆ UWM North, Milwaukee (55-079-0041) 1991-present (carbonyl compounds)
- ◆ UWM North, Milwaukee (55-079-0041) January 1997 - present (VOCs)

The air toxics monitoring network is intended to provide information for the following uses:

- ▶ Determine concentrations of HAPs in Wisconsin's Urban Atmospheres
- ▶ Assess Potential Air Toxics Problems
- ▶ Background Data and Trend Analysis
- ▶ Fate of Air Toxics

The prototype site established in Green Bay had the additional purpose of evaluating various sampling and analytical methodologies. Expansion of toxic monitoring efforts to additional locations is based upon the success and failure of the different methods. The program is considered a screening program because only a few of the large number of potentially toxic compounds are collected and quantified.

Most of these compounds are listed in Table 1 on the following page. Parameters are incorporated into the following groups: semi-volatile organic compounds, non-volatile metals, carbonyls and VOCs.

Table 1: Parameter List for Wisconsin Urban Air Toxics Monitoring Program, 1996 - 97		
<b>SEMI-VOLATILE ORGANIC COMPOUNDS</b>		cis-CHLORDANE
ATRAZINE	HEPTACHLOR EPOXIDE	cis-NONACHLOR
DDE	LINDANE	trans-CHLORDANE
DIELDRIN	TOTAL PCBS (Aroclor)	trans-NONACHLOR
<b>NON-VOLATILE METALS</b>		SELENIUM
ARSENIC	CHROMIUM	VANADIUM
CADMIUM	LEAD	TSP (µg/M3)
<b>CARBONYL COMPOUNDS</b>		
ACETALDEHYDE	ACETONE	FORMALDEHYDE
<b>VOLATILE ORGANIC COMPOUNDS</b>		METHYLCHLORIDE
1,1,1-TRICHLOROETHANE	BROMODICHLOROMETHANE	METHYLENE CHLORIDE
1,1,2,2-TETRACHLOROETHANE	BROMOFORM	n-OCTANE
1,1,2-TRICHLOROETHANE	BROMOMETHANE	o-XYLENE
1,1-DICHLOROETHANE	c-1,3-DICHLOROPROPENE	PROPENE
1,2-DICHLOROBENZENE	CARBON TETRACHLORIDE	STYRENE
1,2-DICHLOROETHANE	CHLOROBENZENE	t-1,2-DICHLOROETHENE
1,2-DICHLOROPROPANE	CHLOROETHANE	t-1,3-DICHLOROPROPENE
1,3-DICHLOROBENZENE	CHLOROFORM	TETRACHLOROETHENE
1,3 BUTADIENE	CHLOROPRENE	TOLUENE
1,4-DICHLOROBENZENE	CUMENE (i-PROPYLBENZENE)	TRICHLOROETHENE
ACETYLENE	DIBROMOCHLOROMETHANE	VINYLCHLORIDE
BENZENE	ETHYLBENZENE	XYLENES (m & p)

This report attempts to incorporate more information about many of parameters evaluated, including parameter sources and uses, along with reported emissions. It is anticipated that future reports will further expand on these additional pertinent topics for all parameters of interest. Results from July 1996 through June 1997 are summarized for all sites and parameters listed above. In addition, metal and carbonyl parameters are subjected to more in-depth analysis, incorporating all results currently available. This is the third report covering activities of the WUATM.

Polychlorinated biphenyl (PCB) values ranged from 0.04 ng/m<sup>3</sup> to 1.30 ng/m<sup>3</sup>, with an average of 0.39 ng/m<sup>3</sup>. PCBs were detected in 91.2% of the samples submitted. These values are consistent with previously observed values. Other semi-volatile organic parameters were detected during the 1996/1997 sampling season, most notably atrazine and lindane, which were present in 41.2% and 61.8% of samples respectively.

Formaldehyde values observed in Green Bay during the 1997 sampling season range from 0.05 µg/m<sup>3</sup> to 1.04 µg/m<sup>3</sup>, with an average of 0.48 µg/m<sup>3</sup>. Formaldehyde is monitored elsewhere in the state as part of the Photochemical Assessment Monitoring (PAMS) program. This report includes an evaluation of 24 hour sample data from Milwaukee between 1992 and June 1997, and a comparison to the Green Bay results during the same period.

A variety of volatile organic compounds considered Toxics have been detected in the atmosphere of

Green Bay. Detected values have ranged from 0.05 ppbv to 3.0 ppbv (maximum value for acetylene). The average values for all parameters other than acetylene are less than 1 ppbv (average acetylene value is 1.34 ppbv). Analysis of canister samples from the Milwaukee PAMS site for toxic VOCs was instated in January 1997. Results from these samples range from 0.05 ppbv to 5.2 ppbv (maximum value for acetylene). The average values for all parameters other than acetylene are less than 1 ppbv (average acetylene is 1.88 ppbv). Although VOC concentrations tend to be highly variable based on location, values obtained in other published air toxic studies are generally in the same order of magnitude as those reported here.

Metal parameters throughout the WUATM program are extensively analyzed in this report. This includes all results from Green Bay and the first year of sampling in Superior, Milwaukee, Waukesha and Trout Lake. Values observed in Green Bay are consistent with other years, while those from the other sites follow the apparent trend of Milwaukee  $\approx$  Waukesha > Green Bay  $\approx$  Superior > Trout Lake.

In summary, the toxics monitoring prototype site in Green Bay provides a significant quantity of information regarding a number of toxic compounds present in the air of this city. Current results can be compared to results obtained during the previous years to provide insight into trends and distribution of HAPS. The expansion of monitoring to a number of additional sites has been successful, with the potential for evaluating differences between various localities apparent.

Although a considerable amount of work has been done to improve the sensitivity and specificity of the methodologies employed by WUATM, additional work remains to be done. Numerous parameters of interest are present in different areas of the state for which there are currently no proven sampling techniques, and for which method development continues.

This document comes to publication more than a year after the latest sampling date reported, during which time a number of changes have occurred within the WUATM program. No attempt has been made to document these changes within the context of this report, as the data through June, 1998 is expected to be published shortly. Recommendations regarding continued operations and expansion of the toxics monitoring network will be incorporated into this later report.



## Sampling and Analytical Procedures

Sampling and analytical procedures for all parameters are specified in the Hazardous Air Contaminants Fixed Urban Site Monitoring Program Quality Assurance Project Plan (QA 8.0) prepared by DNR personnel in 1991. Specific methods are documented in the DNR Air Monitoring Handbook, and are referenced below as “DNR OP” followed by the method number.

### ***Semi-Volatile Organic Compounds: Polychlorinated Biphenyls and Pesticides***

PCB samples are collected using a General Metal Works PS-1 sampler loaded with a combination quartz filter and polyurethane foam (PUF) plug, following EPA TO-4 protocols as outlined in DNR OP 8.5, Sampling Semi-volatile Organic Compounds Using a PS-1 Sampler. Air is drawn through the sampler at the maximum possible rate. This rate varies from slightly over 8 CFM to as much as 9.5 CFM, depending upon the condition of the sampler motor and the density of the PUF plug.

Sampling protocols call for a 72 hour sampling period during the warmer months (April through October), and a 144 hour sampling period for the remainder of the year. The 144 hour sampling period is achieved through 2 separate 3 day sampling periods following the every 12 day sampling schedule.

Following collection of the sample, the filter and PUF plug are packed in hexane rinsed aluminum foil and shipped to the laboratory for analysis. Analysis for these parameters is performed at the State Lab of Hygiene (SLOH). PUF plugs and filters are extracted with 5% ethyl ether/hexane and brought to a final volume of 1 ml. The extracts are analyzed by gas chromatography with an electron capture detector to determine the presence of selected chlorinated compounds. Confirmation of compounds is through the routine use of dual column analysis, with occasional mass spectroscopy.

### ***Polar Organic Compounds: Carbonyls***

Carbonyl samples are collected by drawing a known volume of ambient air through commercially prepared cartridges containing 2,4-dinitro phenylhydrazine (DNPH) coated silica gel, following EPA TO-11 as outlined in DNR OP 8.4, Aldehyde Sampling with 2,4-Dinitro phenylhydrazine impregnated sampling cartridges. Aldehydes react with the DNPH to form stable derivatives which can then be analyzed. Samples are collected over a 24 hour period at a rate of approximately 700 cc/min. Following collection, samples are refrigerated until shipment to the laboratory.

Aldehyde samples are analyzed at the Wisconsin Occupational Health Laboratory (WOHL). The exposed cartridges are washed with acetonitrile to remove the aldehyde-DNPH derivatives. The eluant is brought to a known volume and then analyzed using reversed phase high pressure liquid chromatography (HPLC) coupled with UV absorption detection.

## ***Volatile Organic Compounds***

Sampling and analysis of VOCs follows the protocols of EPA TO-14 employing passivated stainless steel canisters. A low flow 24 hour sample is collected in an evacuated canister, which is then sent to the laboratory for cryogenic concentration followed by gas chromatography with electron capture and flame ionization detection (GC/ECD&FID). The analysis is performed at the SLOH Environmental Studies Unit.

## ***Total Suspended Particulate and Metals***

Standard high volume methods as documented in DNR OP.1.2, High Volume Sampler, are employed at the Green Bay Toxic monitoring sites for the collection of TSP samples. A 24 hour sample is collected on a pre-weighed glass fiber filter at an average flow rate of 1.42 m<sup>3</sup> per minute. Filters are sent to the SLOH for determination of total mass of particulate collected. The same sample is used for determination of ambient concentrations of non-volatile metals. The metals are determined by digesting a portion of the filter in acid and analyzing the resulting solution using atomic absorption spectroscopy.

## ***Quality Assurance Objectives***

Several aspects of quality control and assurance protocols have been incorporated into the WUATM. The quality assurance objectives are precision, accuracy, completeness, representativeness and comparability. Blank sampling materials are analyzed to determine background levels of parameters.

Precision for discrete samples is determined by means of quarterly duplicate samples. The goal is for the duplicates to be within  $\pm 15\%$  for each individual parameter. In the case of metals sampling, a single sample has two separate portions analyzed by the same protocols, rather than two separate samples being submitted to the laboratory.

Accuracy is intended to be determined on two levels, that of sampling using air flow audits, and also analytical accuracy through submission of spiked samples. Sampler audits are performed yearly by personnel other than the regular site operator, with the goal being to have the actual flow rate within  $\pm 10\%$  of the expected sampling air flow rate.

Analytical relative accuracy determinations are made by submitting samples spiked with representative compounds. These samples are occasionally available from EPA and other sources. Several of these samples were submitted. In addition, spiked media recovery determinations are a typical part of the analytical in-house quality control mechanism. The goal for accuracy determinations are for the results to be within  $\pm 25\%$  of the actual amount introduced to the media.

The completeness parameter involves trying to obtain valid samples for all scheduled sampling

days. Monitoring plans called for sampling metals every 6 days until July 1996. The schedule was modified at this time to a one in every 30 days sampling regime. Sampling frequency for carbonyl compounds was similarly reduced to one in every 30 days from a one in every 12 day schedule in July 1996. Semi-volatile and volatile organic compounds remain on an offset every 12 days schedule.

Representativeness is accomplished through meeting the criteria for sampling locations set forth by USEPA in the Compendium of Methods for the Determination of Toxic Organic Compounds and 40 CFR Part 58, Appendix E. In addition, the use of statistics to determine whether sampling frequency changes have affected the representativeness of the data are presented with respect to the expansion of the metals program.

Comparability involves reporting data in units consistent with other organizations reporting similar data. In general, volatile compounds are reported in part per billion volume (ppbv), while semi-volatile and non-volatile compounds are reported in micrograms or nanograms per cubic meter ( $\mu\text{g}/\text{m}^3$  or  $\text{ng}/\text{m}^3$ ).

Background concentrations of parameters on sampling materials can interfere with ambient determinations. Ideally, blank values should be less than the analytical detection limit.

## **Semi-Volatile Organic Compound Parameters**

### ***Overview***

This broad designation includes a wide variety of chemicals, both natural and synthetic. The compounds are generally volatile oils or solids with a low affinity for water, and are represented by a wide variety of individual parameter groups. This variety poses numerous difficulties for an air sampling program. Different collection and analytical methods are suited for different compound classes. Also, many chemicals of potential interest do not have proven methods for their determination in air.

The approach adopted by WUATM has been to employ adsorbent sampling with polyurethane foam (PUF), coupled with a couple of different analytical methods. The first of these analytical methods employs High Pressure Liquid Chromatography (HPLC) with UV Fluorescence detection for the determination of PAH compounds. The second method couples Gas Chromatography (GC) with two different detectors (Electron Capture (ECD) and Nitrogen/Phosphorus (NPD)) to determine PCBs and some pesticides.

Polynuclear aromatic hydrocarbon (PAH) determinations were discontinued in January, 1997 due to consistent quality control difficulties. Results are not presented for this class of compounds because of the unreliability of the data. The difficulties encountered during sampling for these compounds is documented in the previous report (AM-230-97).

Although the 1997 sampling year was the final year of WUATM monitoring for most parameters in Green Bay, PCB and pesticide sampling remained in the area because of concerns related to the Fox River and lower Green Bay. A PUF sampler was located at the Younkers TSP site (AIRS#55-009-0009) on (NAME) Street in May 1997. Samples were collected at both sites during May and June. This report contains PCB and pesticide results from the 1996 - 1997 WUATM project year only. The next data report will document these parameters to a greater extent.

### ***Data Completeness***

PCB and pesticide samples were collected continuously throughout the testing period. Sampling frequency and duration is dependent upon season. 72 hour samples were collected on a 1 in 6 day cycle between July and early November. 144 hour samples were collected on a 1 in 24 day cycle between late November and early April. 72 hour samples were collected on a 1 in 12 day cycle for the remainder of the season.

Project completeness is documented in the following table. In this table, Sampling Completeness is the ratio of Ambient samples collected to total Sampling days. Analytical Completeness in this table is the ratio of Samples to Samples Submitted.

**Table 2: PCB and Pesticides Completeness**

<b>Completeness</b>	<b>Samples</b>	<b>Voids</b>	<b>Ambient</b>	<b>Blanks</b>	<b>Site Comparisons</b>	<b>Duplicates</b>	<b>Sample Days</b>
100.0%	45	5	28	6	3	4	28

### ***Analytical Results***

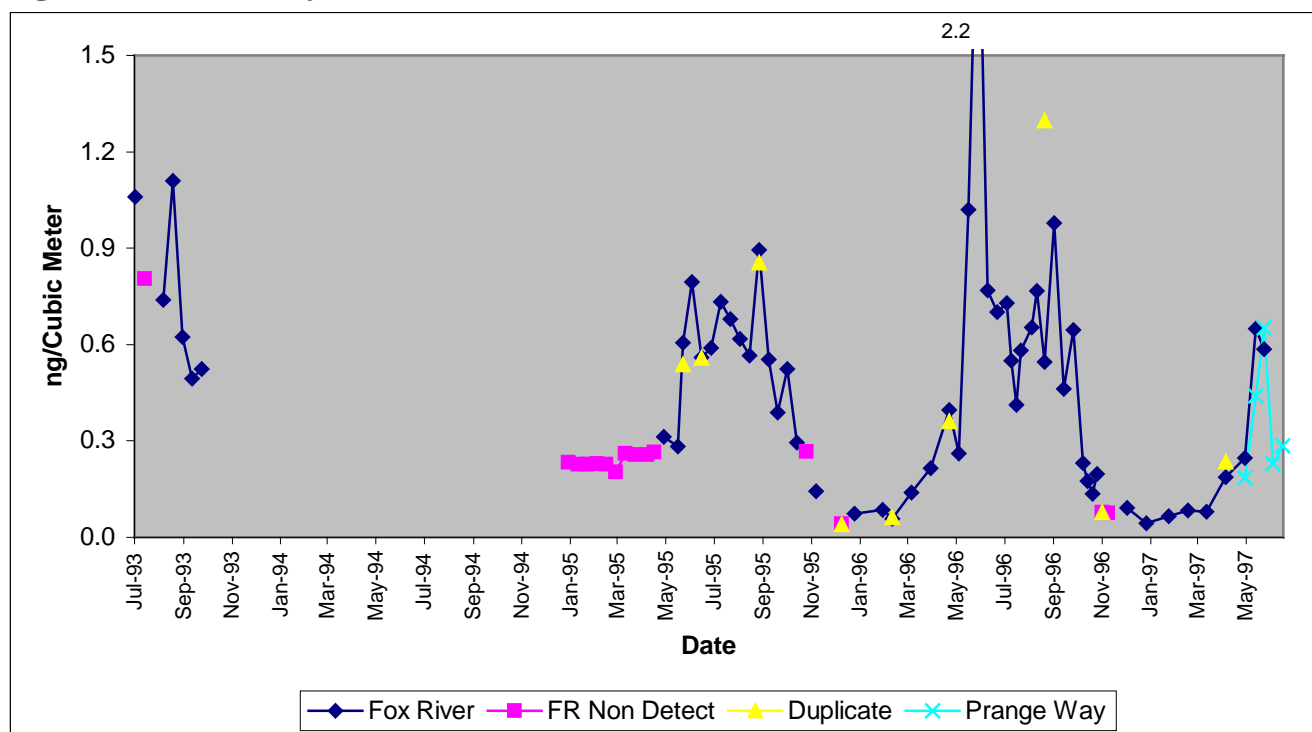
PCB results of all samples were evaluated on the basis of maximum possible values in the case of non-detects, and actual values in the case of detected quantities. Parameters marked with a star (\*) have had analytical reporting limits changed since the values here were reported. The reporting limit has been raised, with the result that only 3 of the values would have been reported under the new protocol (all lindane).

Table 3 below summarizes results for all reported PCB analytical parameters. Values are reported in ng/m<sup>3</sup>. PCB results from 1993 forward are shown graphically in Figure 1. It should be noted that a significant gap in the historic data is present. No samples were collected between November 1993 and December 1995, due to a variety of reasons including difficulties in obtaining sampling materials and site operator errors.

**Table 3: PCB and Pesticide Results (ng/m<sup>3</sup>)**

Parameter	Average	Maximum	Minimum	RSD(%)	Detects	Reported	% Detect
TOTAL PCBS (Aroclor)	0.39	1.30	0.04	77.5%	31	34	91.2%
ATRAZINE	0.23	0.60	0.07	54.6%	14	34	41.2%
cis-CHLORDANE *	0.02	0.05	0.01	92.2%	2	34	5.8%
trans-CHLORDANE *	0.01	0.02	0.01	90.7%	5	34	14.7%
DDE *	0.02	0.05	0.01	92.2%	4	34	11.8%
DIELDRIN *	0.03	0.12	0.01	63.2%	1	34	2.9%
HEPTACHLOR EPOXIDE *	0.02	0.05	0.01	89.6%	2	34	5.8%
LINDANE *	0.02	0.05	0.01	69.9%	21	34	61.8%
trans-NONACHLOR *	0.02	0.05	0.01	93.6%	1	34	2.9%

**Figure 1: Green Bay PCB Results, 1993 - 1997**



### Quality Assurance Parameters

Duplicate precision is reported for samples wherein detects were noted. A total of 3 successful duplicate samples were collected. Out of a total of 30 data pairs, there were no bad pairs, 25 non-detect pairs (83.3%), and 5 detect pairs (16.7%). All PCB data, and detect data pairs are shown in the table below. It should be noted that the duplicate sample on 8/31/96 ran for only 24 hours. Results from these two samples are significantly different. The relative standard deviation from these samples is not included in the QA determination because of the differences in sample time.

The differences could arise through a couple of different means. Most of the loading of the sample could have occurred during the first day (when both samplers were running), which would imply that the results are indicative of ambient conditions. The other obvious option is volatilization of PCBs off the sampling material during the 72 hour sampling run. Sample recovery tests conducted every other year appear to indicate minimal sample loss under these conditions.

**Table 4: PCB and Pesticide Duplicates (ng/m<sup>3</sup>)**

Parameter Name	Sample Date	Primary	Duplicate	Average	% Diff	Detects
TOTAL PCBS (Aroclor)	04/16/97	0.19	0.23	0.21	22.4%	Y/Y
<b>TOTAL PCBS (Aroclor)</b>	<b>08/31/96</b>	<b>0.55</b>	<b>1.30</b>	<b>0.92</b>		<b>Y/Y</b>
TOTAL PCBS (Aroclor)	11/11/96	0.08	0.08	0.08		N/N
ATRAZINE	04/16/97	0.17	0.16	0.17	5.6%	Y/Y
LINDANE	08/31/96	0.01	0.03	0.02	100.0%	Y/Y
LINDANE	04/16/97	0.04	0.04	0.04	4.1%	Y/Y

A total of 5 blank samples had results returned. No parameters were detected in any of these samples.

### ***Polychlorinated Biphenyls and Pesticides Inter Site Comparison***

Three samples were collected concurrently at each of the sites in Green Bay to determine whether there was an observable difference between the two sites. Detected results from these samples are documented in the table below. Note that the average percent difference between the PCB and atrazine values is only slightly larger than the duplicate samples. All PCB data from 1993 on will be subjected to detailed statistical analysis in the next report.

**Table 5: Inter Site PCB Comparisons**

Parameter Name	Sample Date	Fox River	Younkers	Average	% Diff	Detects
TOTAL PCBS (Aroclor)	05/10/97	0.25	0.19	0.22	28.4%	Y/Y
TOTAL PCBS (Aroclor)	05/24/97	0.65	0.44	0.54	38.5%	Y/Y
TOTAL PCBS (Aroclor)	06/03/97	0.59	0.65	0.62	10.7%	Y/Y
<b>Average</b>					25.9%	
ATRAZINE	05/10/97	0.27	0.25	0.26	7.4%	Y/Y
ATRAZINE	05/24/97	0.23	0.22	0.22	4.5%	Y/Y
ATRAZINE	06/03/97	0.33	0.29	0.31	12.9%	Y/Y
<b>Average</b>					8.2%	

## **INORGANIC PARAMETERS**

### ***Overview***

This report incorporates all metals results and the associated TSP data collected during WUATM sampling statewide. Samples were collected in Green Bay from the Bay Beach site (July 1991 - January 1993); and the Fox River site (April 1993 - June 1997). Metals determinations were expanded from Green Bay to 4 additional sites around the state in July 1996. Three of these sites are located in other urban areas (Superior, Milwaukee and Waukesha), while the fourth is a remote background station located in the Northern Highland American Legion State Forest at Trout Lake. All sites selected were previously established TSP monitoring sites. The 96/97 sampling season marks the end of the current metal sampling in Green Bay.

The historical data can not only be used for trend analysis, but provides a body of information against which the representativeness of our current sampling frequency can be evaluated. Multiple sites allow for more meaningful evaluation of the data, in the sense of divining whether observed concentrations are typical for urban areas. The addition of a background site introduces the potential to determine the impact urban zones are having with respect to these parameters in the ambient air.

Background information on the uses, atmospheric sources and reported emissions in Wisconsin are included along with the basic data collected as part of WUATM. This data is presented in several sections. The first of these deals with the basic results and quality control summary of the current monitoring period. This is followed by an in depth initial evaluation of the regional variations present in the data. It should be noted that with the current level of sampling, yearly and site differences will be more difficult to discern and subject to higher levels of uncertainty. The final section presents an in-depth analysis of the Green Bay data by parameter across the entire project.

### ***Parameter Uses and Atmospheric Sources***

The metals chosen for this work (arsenic, cadmium, chromium, lead, selenium and vanadium) are all naturally occurring elements, and have potential natural sources, such as volcanic eruptions (which are capable of dispersing particles world-wide), forest fires and wind entrainment of mineral bearing soils. Each of the elements also has significant anthropogenic sources, including the manufacture, use and disposal of products containing them, combustion processes and development pressures increasing the prevalence of erosion and wild fires. In general, the fate of these elements' emissions is wind dispersal and subsequent wet or dry deposition.

Arsenic is used primarily as a wood preservative and in agricultural chemicals (insecticides, herbicides, algacides, and growth stimulants). These uses accounted for about 93% of the total

consumption in the United States around 1990. Smaller amounts were also used in the production of glass and nonferrous alloys, and in the electronics industry. Releases of arsenic to the atmosphere can come from production of any of the above materials, combustion of coal or treated lumber, and use of arsenic containing chemicals. Primary atmospheric sources in Wisconsin are fossil fuel combustion related.

Cadmium is a heavy metal that is used mainly in batteries, pigments, metal coatings, plastics and alloys. One compound (cadmium sulfide) has been used in the conversion of solar energy to electrical power. Some cadmium compounds are used as fungicides for golf courses and home lawns. Metal production, industrial applications, manufacture of phosphate fertilizers, and coal, wood, and oil combustion are major contributors of cadmium to the atmosphere. Principal cadmium sources in Wisconsin include fossil fuel combustion, waste incineration and metals processing.

Chromium's fundamental uses are in the metallurgical, refractory and chemical industries. It is used to produce stainless steels and various alloys, with typical materials ranging from 11.5% to 30% chromium by weight. Chromium bearing materials have a strong heat resistance, and find use as linings for high temperature industrial furnaces. Other uses include pigments, metal finishing, leather tanning, catalysts and wood preservatives.

Primary emission sources include the metal industries and fossil fuel combustion, accounting for about 45% and 26% to 45% of the total. A wide variety of minor sources are associated with the various uses and disposal of chromium bearing products. Principal atmospheric sources in Wisconsin include fuel combustion and metals processing.

Lead is a metal that has been widely used and dispersed into the environment since at least ancient Roman times. Recent uses with major environmental consequences that have been discontinued include gasoline additives and paint pigments. These uses have left a legacy of increased lead content in roadside dusts and in older houses. About 80% of lead used during 1990 was in lead-acid storage batteries.

Estimates of emissions on a national level indicate that between 1992 and 1995, industrial processes were responsible for about 60% of total emissions, with metals processing, recycling and waste incineration accounting for the majority of this. Transportation and combustion processes were responsible for about 25% and 10% , respectively, of the total estimated emissions. Greater than 30% of reported toxic metal emissions for all parameters in this study between 1992 (the first year this source reported) and 1996 originate from a single lead source.

Selenium compounds are common and can be found in most rocks and soils. Selenium in the elemental form is rare, however, being obtained primarily as a byproduct of copper smelting. The element's photoelectric and semi-conductor properties make it useful for a wide variety of photo and xerographic applications. These uses accounted for almost half of the total processed in 1983. The glass industry consumes a significant quantity of selenium for tinting glass, and with other pigmentation applications accounts for another 40% of the annual demand for these compounds. A variety of uses including catalysis, and medical and nutritional preparations account for the remaining 10 - 15%.



The major source of anthropogenic Selenium in the atmosphere is combustion of coal and other fossil fuels. Estimates of the quantity of releases from these sources vary between about 1,000 and 2,000 tons per year nationwide. Additional sources include industrial and municipal waste incineration, along with primary production and processing of selenium containing materials. Natural sources of selenium to the atmosphere include microbial and plant action, which convert the element to volatile compounds, and volcanic gases. The magnitude of these sources is not known, although some estimates of the releases rival that of the anthropogenic sources. Principal selenium sources in Wisconsin are fossil fuel combustion related.

Vanadium is present throughout the earth's crust at an average concentration of 150 mg/kg (150 ppm by weight). Its uses are primarily in metallurgical applications, including alloying in steel, ferrovanadium alloys, and nonferrous titanium alloys. Minor uses include industrial catalyst applications, driers in paints and varnishes and as components in photographic developers. Atmospheric sources of this element include combustion of fossil fuels, especially fuel oils, and primary production of vanadium containing materials. Natural sources include continental dust, marine aerosol and volcanic eruptions. Few sources in Wisconsin report this parameter. Most of them are fossil fuel combustion related.

### ***Reported Emissions***

Industrial sources that emit quantities of toxic materials above set limits are required to report their emissions to the DNR. Reporting requirements have varied over the years, both in reporting limits and targeted compounds. In addition, recognition of all sources that should be reporting may not be complete. As such, it is important to note that the data in the tables below should be used only as a rough guideline for total emissions of these six metals. Table 9 below lists the reporting limits for these parameters.

Reported toxic releases for each of the parameters statewide between 1990 and 1996 are summarized in the tables below. The first table lists the number of reporting sources and emissions. The second table summarizes these emissions by the size of the source (greater than 1000 pounds per year and greater than 100 pounds per year). This table has been included to illustrate that a relatively few sources are responsible for the majority of reported metals emissions in the state. That the single largest reporting source started reporting in 1992 illustrates both points. The third table summarizes reported emissions for Brown County.

**Table 6: Reported Industrial Emissions of Study Metals in Wisconsin**

Toxic Compound	Data	1996	1995	1994	1993	1992	1991	1990
<b>Arsenic and compounds, as As</b>	Sources	73	74	91	85	181	175	162
	Emissions (lb/yr)	4789	4202	7490	14827	15208	16759	20966
<b>Cadmium and compounds, as Cd</b>	Sources	74	73	85	78	190	178	169
	Emissions (lb/yr)	2621	1856	1719	1862	11510	3152	3686
<b>Chromium and compounds, as Cr</b>	Sources	88	86	110	117	248	250	226
	Emissions (lb/yr)	25307	23660	24671	20380	20712	31388	37616
<b>Lead and Compounds, as Pb</b>	Sources	26	24	16	19	18	1	
	Emissions (lb/yr)	49969	68789	48432	39805	28904	275	
<b>Selenium and compounds, as Se</b>	Sources	38	50	46	34	85	87	90
	Emissions (lb/yr)	7562	7719	2848	8890	4486	8486	12230
<b>Vanadium, as V2O5</b>	Sources	3	2	4	11	14	10	
	Emissions (lb/yr)	1600	1428	1858	6421	5576	1618	
<b>Total Count of Sources</b>		302	309	352	344	736	701	647
<b>Total Sum of Emissions (lb/yr)</b>		91848	107654	87018	92184	86395	61678	74498

**Table 7: Major Source Contributions to Reported Wisconsin Metal Emissions**

<b>Highest Single Source, Percent of Total</b>		29.8%	31.5%	42.2%	34.2%	32.2%	7.0%	5.8%
<b>Sources Reporting &gt;1000 Lbs</b>	Sources	14	8	12	15	17	19	24
	Emissions (lb/yr)	68670	82324	67380	66874	62121	36868	46571
<b>Percent of Total</b>	Sources	4.6%	2.6%	3.4%	4.4%	2.3%	2.7%	3.7%
	Emissions (lb/yr)	74.8%	76.5%	77.4%	72.5%	71.9%	59.8%	62.5%
<b>Sources Reporting &gt;100 Lbs</b>	Sources	70	71	56	81	77	79	82
	Emissions (lb/yr)	89036	105302	83143	88485	81498	56731	69100
<b>Percent of Total</b>	Sources	23.2%	23.0%	15.9%	23.5%	10.5%	11.3%	12.7%
	Emissions (lb/yr)	96.9%	97.8%	95.5%	96.0%	94.3%	92.0%	92.8%

**Table 8: Reported Brown County Emissions (lb/yr)**

Parameter	1990	1991	1992	1993	1994	1995	1996	Grand Total
<b>Arsenic and compounds, as As</b>	2859	1966	694	407	607	643	326	7501
<b>Cadmium and compounds, as Cd</b>	1015	954	900	31	56	76	91	3122
<b>All Chromium forms and compounds, as Cr</b>	7192	6635	235	30	1172	1185	1178	17628
<b>Lead compounds</b>	0	0	216	77	0	0	516	810
<b>Selenium and compounds, as Se</b>	451	356	388	378	1596	202	202	3573
<b>Grand Total</b>	11517	9910	2433	923	3431	2106	2313	32633

**Table 9: Emission Reporting Limits (lb/yr)**

Reporting Limits	1992	1993 - 1997
<b>Arsenic and inorganic compounds, as As</b>	2.5	12
<b>Cadmium and cadmium compounds, as Cd</b>	2.5	12
<b>Chromium (II) compounds, as Cr</b>	357.4	179
<b>Chromium (III) compounds, as Cr</b>	357.4	179
<b>Chromium (VI) compounds, as Cr, water soluble</b>	35.7	18
<b>Chromium (VI) compounds, as Cr, water insoluble</b>	0.2	1

<b>Chromium (metal)</b>	357.4	179
<b>Lead compounds</b>	2000	6000
<b>Selenium and compounds, as Se</b>	145.1	73
<b>Vanadium, as V2O5, respirable dust and fumes</b>	357.4	179

## ***Current TSP and Metals***

### **Data Completeness**

Previous protocols called for the collection of samples on a one in six day schedule, for a total of 60 samples from the Fox River Site. The addition of new sites without additional funding has led to a decrease in the frequency of sampling to a one in thirty day schedule. With five sites, a total of 60 samples could have been analyzed. This choice has the side effect of reducing the certainty of our average observations and increasing the standard error. An evaluation of the representativeness of our current data set with the respect to historic data is discussed with the Green Bay project results.

Project completeness with reference to TSP and metals is documented in the following table. In this table, Completeness is the ratio of valid ambient samples that were analyzed for metals, to total Sampling days. A total of 55 valid sets of metals analysis were obtained from the lab, for an overall completeness of 91.7%. Reasons for missing samples and analysis of void samples may include sampler failures, and laboratory miscommunications.

**Table 10: Statewide Metals Completeness by Site**

<b>Site</b>	<b>Completeness</b>	<b>Valid</b>	<b>Samples</b>	<b>Void</b>	<b>Sampling Days</b>
<b>Green Bay</b>	91.7%	11	11	0	12
<b>Superior</b>	100.0%	12	12	0	12
<b>Milwaukee</b>	83.3%	10	11	1	12
<b>Trout Lake</b>	100.0%	12	12	0	12
<b>Waukesha</b>	83.3%	10	10	0	12
<b>Total</b>	91.7%	55	56	1	60

### **Analytical Results**

Results for TSP and metals analysis for all sites are presented in the following tables. Values reported are in  $\mu\text{g}/\text{m}^3$  for TSP and  $\text{ng}/\text{m}^3$  for metal parameters. Averages, maxima, minima and percent relative standard deviations are shown, along with the number of samples, the number of detects per parameter and the resulting % detection. Non-detects are valued at the detection limit to generate maximum potential concentrations for the evaluation of health risks.

**Table 11: Green Bay Metals (Fox River Site) (ng/m<sup>3</sup>, except for TSP in µg/m<sup>3</sup>)**

Parameter Name	Average	Maximum	Minimum	%RSD	Samples	Detects	% Detection
Arsenic	1.18	2.50	0.54	56.8%	11	8	72.7%
Cadmium	0.52	1.53	0.21	74.2%	11	11	100.0%
Chromium	2.56	4.34	1.07	38.0%	11	11	100.0%
Lead	9.77	22.78	2.15	72.2%	11	11	100.0%
Selenium	1.18	2.57	0.54	64.0%	11	6	54.5%
Vanadium	1.57	2.71	1.03	34.7%	11	8	72.7%
TSP	51	124	10	65.7%	12	12	100.0%

**Table 12: Superior Metals (Winter Street Site) (ng/m<sup>3</sup>, except for TSP in µg/m<sup>3</sup>)**

Parameter Name	Average	Maximum	Minimum	%RSD	Samples	Detects	% Detection
Arsenic	1.18	3.20	0.52	62.4%	12	10	83.3%
Cadmium	0.70	4.95	0.10	194.6%	12	12	100.0%
Chromium	3.05	5.20	1.09	46.3%	12	11	91.7%
Lead	12.10	39.34	2.61	81.1%	12	12	100.0%
Selenium	0.73	2.25	0.51	70.0%	12	4	33.3%
Vanadium	2.44	4.30	1.02	55.6%	12	9	75.0%
TSP	49	101	14	49.3%	12	12	100.0%

**Table 13: Milwaukee Metals (Greenfield Avenue Site) (ng/m<sup>3</sup>, except for TSP in µg/m<sup>3</sup>)**

Parameter Name	Average	Maximum	Minimum	%RSD	Samples	Detects	% Detection
Arsenic	1.89	3.50	0.56	44.6%	10	10	100.0%
Cadmium	0.73	1.94	0.23	66.2%	10	10	100.0%
Chromium	6.30	20.70	1.83	95.1%	10	10	100.0%
Lead	22.25	49.50	7.32	57.6%	10	10	100.0%
Selenium	1.69	2.97	0.55	61.8%	10	6	60.0%
Vanadium	2.91	6.20	1.13	61.9%	10	7	70.0%
TSP	53	119	16	54.0%	11	11	100.0%

**Table 14: Waukesha Metals (Melendez Site) (ng/m<sup>3</sup>, except for TSP in µg/m<sup>3</sup>)**

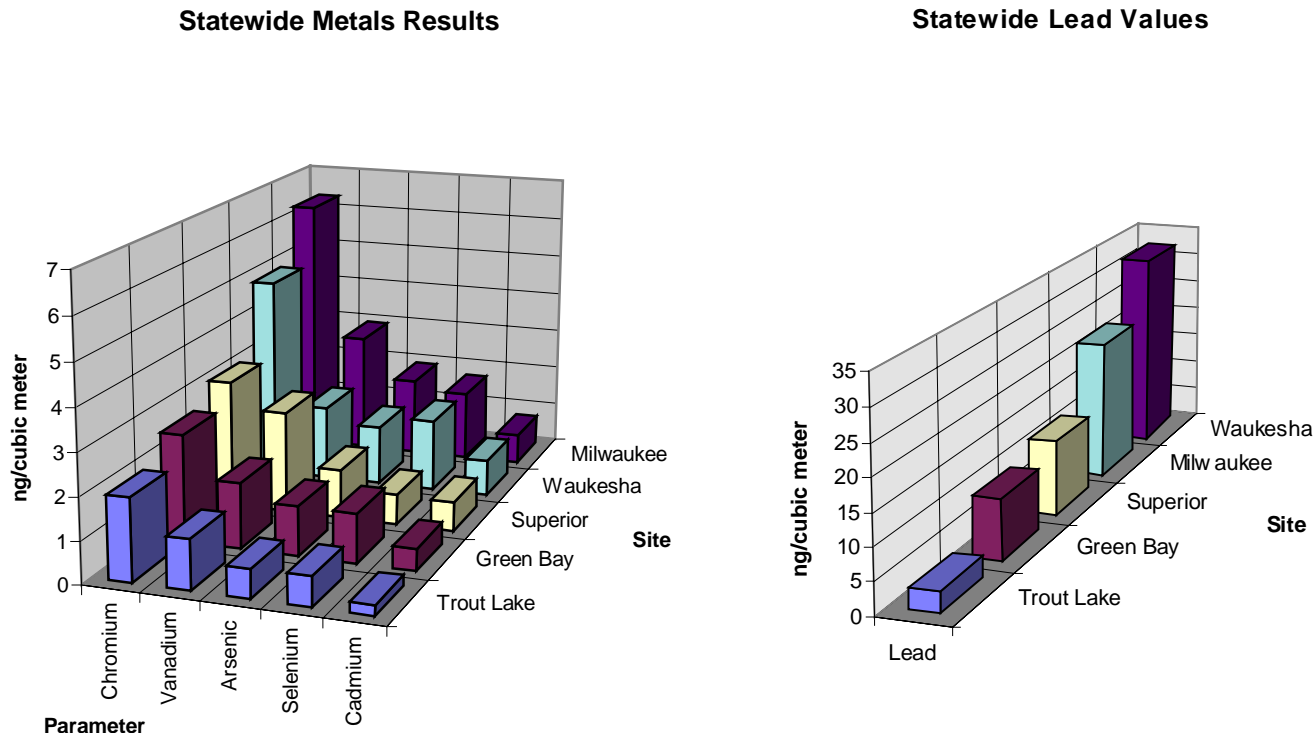
Parameter Name	Average	Maximum	Minimum	%RSD	Samples	Detects	% Detection
Arsenic	1.44	2.28	0.59	37.2%	10	9	90.0%
Cadmium	0.87	2.66	0.19	91.5%	10	10	100.0%
Chromium	4.89	7.98	2.42	39.7%	10	10	100.0%
Lead	32.15	75.40	6.49	73.5%	10	10	100.0%
Selenium	1.74	4.47	0.55	78.5%	10	7	70.0%
Vanadium	1.80	2.80	1.12	36.4%	10	8	80.0%
TSP	60	117	18	56.8%	10	10	100.0%

**Table 15: Background Metals (Trout Lake Site) (ng/m<sup>3</sup>, except for TSP in µg/m<sup>3</sup>)**

Parameter Name	Average	Maximum	Minimum	%RSD	Samples	Detects	% Detection
Arsenic	0.69	1.19	0.53	33.6%	12	4	33.3%
Cadmium	0.25	0.43	0.10	44.9%	12	12	100.0%
Chromium	1.96	3.30	1.08	45.1%	12	6	50.0%
Lead	3.43	10.71	0.57	86.2%	12	11	91.7%
Selenium	0.71	1.19	0.53	36.5%	12	4	33.3%
Vanadium	1.18	1.70	1.05	14.3%	12	1	8.3%
TSP	13	27	2	62.5%	11	11	100.0%

The average values for each parameter except TSP are portrayed in the following graphs.

**Figure 2: Statewide Metal Results, by site and parameter**



## Quality Assurance Parameters

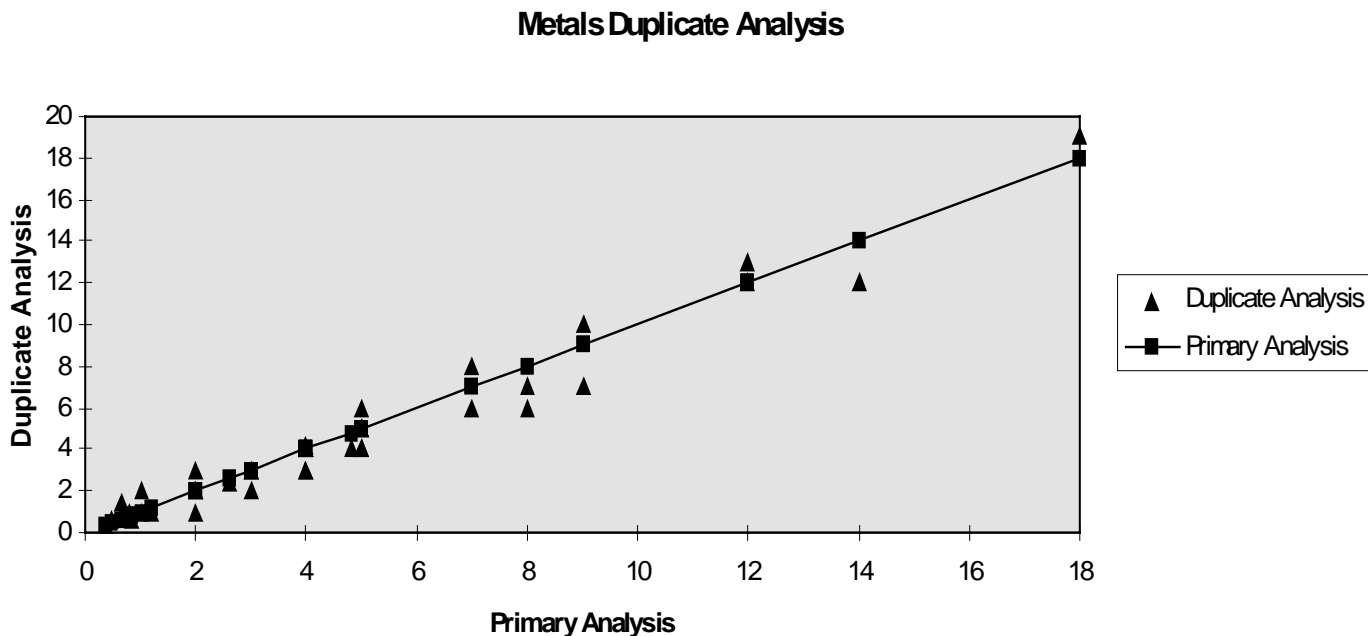
Quality assurance parameters reported by the laboratory include a total of nine filters analyzed in duplicate. Results from these samples are summarized below. There were no blank or split spiked samples reported this year. Please note that the data is in  $\mu\text{g/Liter}$  of solution. Common factors (dilution factor and sample volume) allow for the direct application of the percentage differences to general metals determinations.

Duplicate analysis show a total of 54 data pairs, of which 5 (9.3%) are non-detect pairs with qualitative agreement. A total of 3 pairs (5.6%) show a single detect at the detection limit, while the duplicate analysis yields a non-detect. These values are considered qualitatively the same. A single pair (1.9%) is classified as a “bad pair”, where one of the analysis showed a definitely detectable quantity, and the other didn’t. Of the remaining 45 (83.3%) detect pairs, 9 (16.7%) show a greater than  $\pm 25\%$  difference. The overall average percent difference between duplicate analysis is 15.2%.

This value is increased in comparison with the previously reported value of  $\pm 14.3$ , and is slightly

outside of the QA/QC goal of  $\pm 15\%$ . At the current time it is not possible to determine whether the differences exist in the lab (through variable analytical recovery of parameters) or whether the values represent variable concentrations of the metals on the filter material itself. Values presented are based on the reported values, without further reference to the  $\pm 15\%$  built into the method.

**Figure 3: Comparison of Primary and Duplicate Analyses**



### Data Representativeness

A major concern with the current data is the representativeness of our data set with the decrease in sampling frequency. We have two major ways of evaluating this parameter. One is by comparing the current Green Bay data to that of previous years (discussed with the Green Bay data evaluation), while the other is comparing TSP results for the metals samples with the overall TSP results by site. Each of the new sites collected samples on a one in six day or one in three day schedule. All sites except the Winter street site in Superior collected these samples year round (regular TSP sampling at Winter street was discontinued at the end of December).

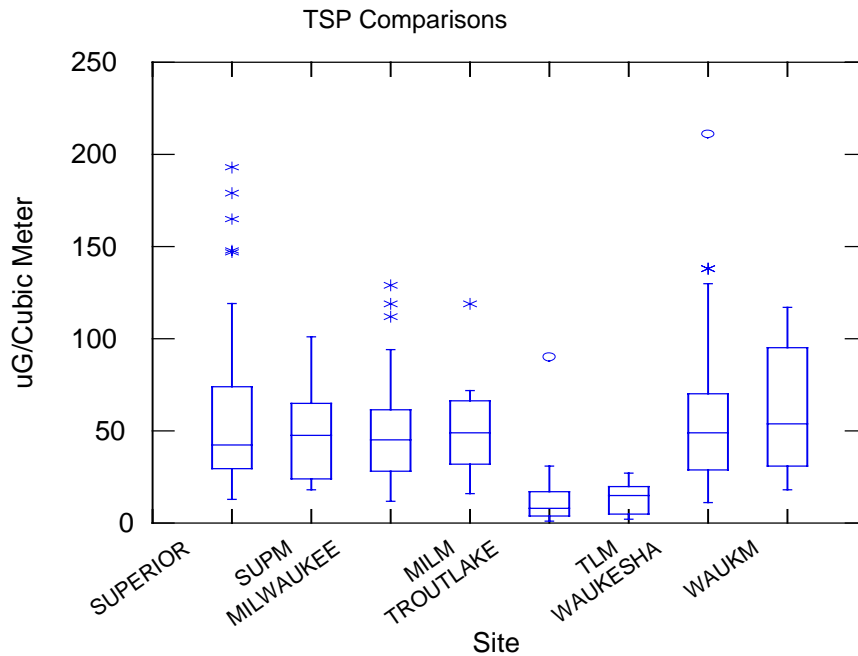
The table below summarizes the TSP data by site. In all cases, the average  $\pm$  the standard error of the metal sample TSP results encompasses the average of the total TSP data set, implying that the smaller set adequately represents the mean of the total population. The representativeness of the data is further examined through graphically representing the metals TSP subset alongside the overall TSP data in a box plot and in distribution graphs. In all of these representations, the data appear to show that the samples chosen for metals analysis are adequately representative of

typical TSP samples collected from the sites.

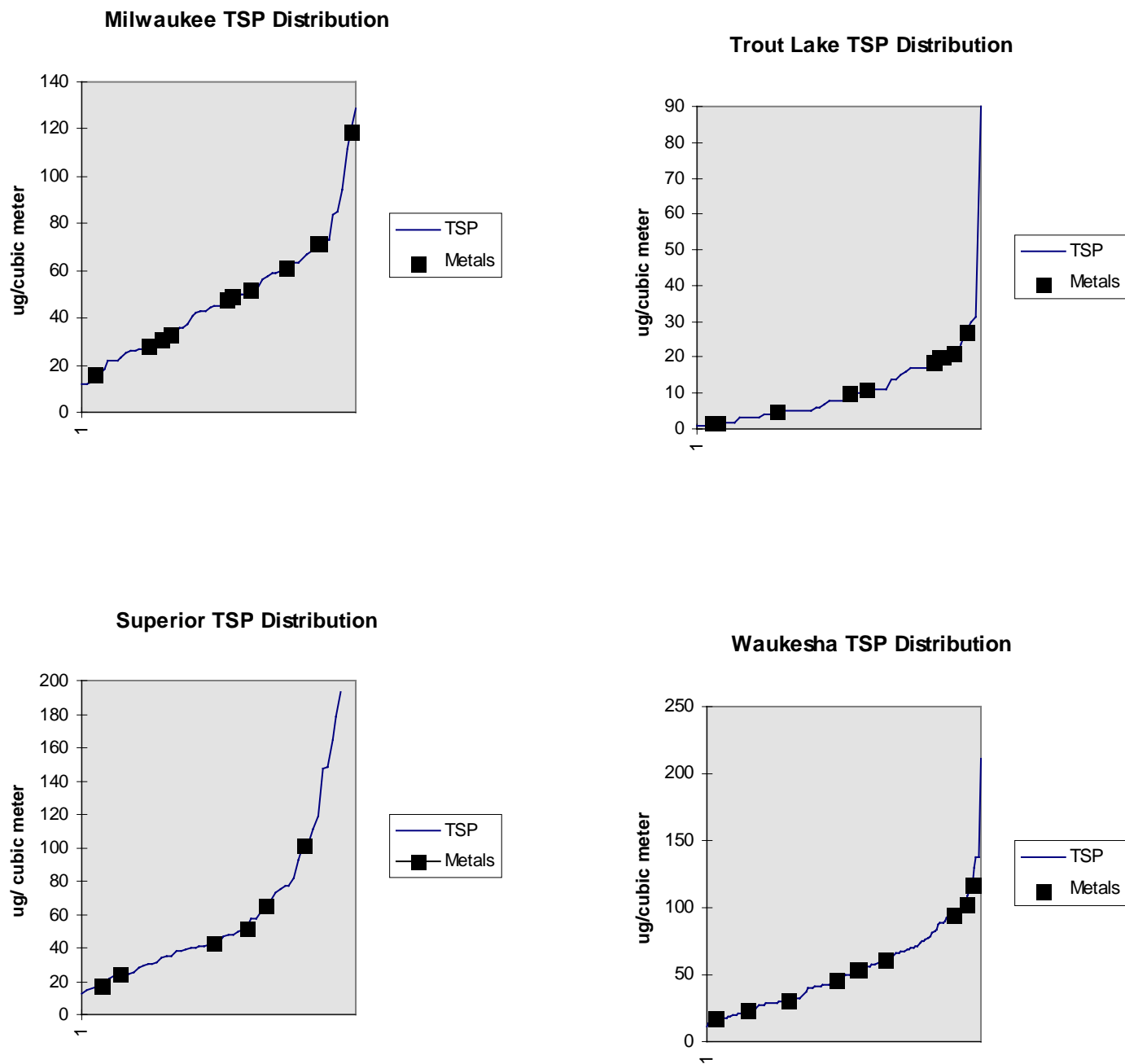
**Table 16: Statewide TSP Comparisons for Representativeness of Metals Sampling Protocol**

Site	Average	Maximum	Minimum	Std Err	Std Dev	Samples
Superior (6 month metals)	51	101	18	12	30	6
Superior	58	193	13	6	43	56
Milwaukee (metals)	53	119	16	9	29	11
Milwaukee	48	129	12	3	25	63
Trout Lake (metals)	13	27	2	3	8	11
Trout Lake	11	90	1	2	13	61
Waukesha (metals)	60	117	18	11	34	10
Waukesha	54	211	11	3	32	131

**Figure 4: Box Plot Relating Site TSP Values to Site Metal Sample TSP Values**



**Figure 5: Distribution of Metals Samples Among TSP Samples**





## Statewide Comparisons

It is important to note that with the current amount of data collected at these sites, values are generally subject to a lessened statistical confidence level. With this in mind, it is especially interesting to note that there are statistically significant differences between many of the sites. Examining the graphs in figure 2 reveals a basic trend of increasing values in the more populated areas. A variety of approaches have been employed to examine the results to determine what significant differences exist between the sites. All statistical manipulations were made using the System for Statistics (Systat), version 7.0.

Among these efforts are ranking of the results from highest to lowest, both as averages and on each individual sampling day. The tables below illustrate these rankings. Trout Lake averages are generally less than the averages for all parameters at the other sites, while Milwaukee and Waukesha sites tend to be the highest.

**Table 17: Parameter by Site Averages Comparison**

Parameter	Ranking Based on Site Average Concentrations					
<b>Arsenic</b>	Milwaukee	>	Waukesha	≥	Superior	≈ Green Bay > Trout Lake
<b>Cadmium</b>	Waukesha	≥	Milwaukee	≈	Superior	≈ Green Bay ≥ Trout Lake
<b>Chromium</b>	Milwaukee	≥	Waukesha	>	Superior	≈ Green Bay ≥ Trout Lake
<b>Lead</b>	Waukesha	>	Milwaukee	>	Superior	≥ Green Bay > Trout Lake
<b>Selenium</b>	Waukesha	≈	Milwaukee	>	Green Bay	≥ Superior = Trout Lake
<b>Vanadium</b>	Milwaukee	≥	Superior	>	Waukesha	≈ Green Bay > Trout Lake

This trend continues when individual samples are compared with the other samples collected during the same month. The categories of the second table below include “tied minimum”, which are mostly evidence of multiple non-detects in a particular group of samples. Only the cadmium results contain a significant portion of the samples from Trout Lake greater than the minimum result obtained during a particular month. It should be noted that not all samples were collected on the same days.

**Table 18: Trout Lake Monthly Minimum Sample Value Counts**

Parameter	Min	Tied Min	> Min
<b>Arsenic</b>	7	4	1
<b>Cadmium</b>	6		6
<b>Chromium</b>	8	3	1
<b>Lead</b>	12		
<b>Selenium</b>	1	8	3
<b>Vanadium</b>	5	6	1

The magnitude of differences with respect to Trout Lake was determined using the ratios of the average parameter value and that of Trout Lake for each parameter and site. Results of this are

tabulated below. All instances where parameter concentrations average greater than twice those observed at Trout Lake are boldfaced. These account for 80% of the observations.

**Table 19: Site to Trout Lake Ratios**

	Green Bay	Superior	Milwaukee	Waukesha
ARSENIC	1.7	1.7	<b>2.8</b>	<b>2.1</b>
CADMIUM	<b>2.1</b>	<b>2.9</b>	<b>3.0</b>	<b>3.6</b>
CHROMIUM	1.3	1.6	<b>3.2</b>	<b>2.5</b>
LEAD	<b>2.9</b>	<b>3.5</b>	<b>6.5</b>	<b>9.4</b>
SELENIUM	1.7	1.0	<b>2.4</b>	<b>2.4</b>
VANADIUM	1.3	<b>2.1</b>	<b>2.5</b>	1.5

In addition to these qualitative tests, statistical significance testing was performed using ANOVA coupled with Fisher's Least-Significant-Difference test. A total of 54 degrees of freedom (4 and 50) are present in the current data set. Significant differences were seen among all parameters except cadmium (F-ratio = 1.089). It is interesting to note that several of the statistically significant ratios between site averages are less than those obtained for cadmium, which are not statistically significant. Part of this is the generally low concentrations of cadmium present at all sites. It is expected that as the size of the data set increases over time, the differences will increase in significance (if not in magnitude). Differences between sites shown to be significant through ANOVA are tabulated below, with corresponding F-ratios and p values.

**Table 20: ANOVA Values for Statewide Metals Comparisons**

	Green Bay	Superior	Trout Lake	Waukesha
<b>ARSENIC</b>	F = 5.248		p < 0.005	
Milwaukee	0.013	0.011	0.000	
Waukesha			0.008	
<b>CHROMIUM</b>	F = 4.325		p < 0.005	
Milwaukee	0.004	0.010	0.001	
Waukesha			0.019	
<b>LEAD</b>	F = 8.387		p < 0.005	
Milwaukee	0.030		0.000	
Waukesha	0.000	0.001	0.000	
<b>SELENIUM</b>	F = 3.767		p < 0.010	
Milwaukee		0.011	0.010	
Waukesha		0.007	0.007	
<b>VANADIUM</b>	F = 4.655		p < 0.005	
Milwaukee	0.006		0.000	0.024
Superior			0.006	

This table presents Anova data listed by parameter. The first row indicates the overall F and p values obtained from the analysis. The following two rows provide a matrix in combination with the four columns to indicate the individual probabilities that overall results from a particular site are different from another.

The development of statistically significant differences between sites with the currently small quantity of data indicates the potential of evaluating the impacts of various anthropogenic sources for the parameters in question. This application of the data will be further investigated as more data is collected.

## **Green Bay Metals**

### **Introduction**

The data collected during this period represents the completion of WUATM's metals sampling in Green Bay. Current and historic Green Bay data is compiled for project closure, and statistical analysis conducted to evaluate any potential trends. All data has been thoroughly checked and verified, with the result that a few values previously reported have been invalidated. These values are noted and explained in the individual parameter discussion. In addition, several samples considered void for TSP purposes because the sampler started at the wrong time have been incorporated for the metals analysis.

It should be noted that unusual values are not excluded simply because they are different from the rest of the data set. The philosophy incorporated into WUATM data analysis is that values provided by the lab are correct and reflect actual environmental conditions, unless a clear reason that said values should be excluded exists (such as insufficient sampling time, indeterminate sample volume or documented analytical difficulties).

Current values from Green Bay fall within the range of previously observed values, with no new maximum or minimum values seen. As such, it appears that decreasing the sample frequency has not affected the general representativeness of our data set, beyond increasing the uncertainty of our measurements.

There are two main factors that complicate the interpretation of this data set: the use of two distinct sampling locations, and an improvement in detection limits. Although the sampling sites (Bay Beach and the Fox River site) were located within 2 miles of each other, there is potential for real differences to exist between them. Evaluation of whether this is the case or not is complicated by the fact that the samples from Bay Beach were analyzed under less stringent protocols and correspondingly higher detection limits.

Detection limits over the course of the project are shown in the table below. It should be noted that these represent analytical limits ( $\mu\text{g/L}$  of solution). The ambient concentrations determined from the analytical results are dependent on the air volume sampled.

**Table 21: Analytical Detection Limits ( $\mu\text{g/L}$ )**

<b>Parameter</b>	<b>Before 1994</b>	<b>After 1994</b>	<b>Parameter</b>	<b>Before 1994</b>	<b>After 1994</b>
<b>Arsenic</b>	3	1	<b>Lead</b>	3	1
<b>Cadmium</b>	0.2	0.08	<b>Selenium</b>	3	1
<b>Chromium</b>	3	2	<b>Vanadium</b>	10	2

The improvement in detection limits is most noticeable with arsenic, selenium and vanadium. Over the course of this project, individual rates of detection for these species ranged from 5.0% - 83.3%, 10.7% - 75.0%, and from 0% - 75.0%, respectively. Incorporation of non-detects into a

data set requires assumptions regarding the numerical value represented by the non-detect. The data for these three parameters are treated with extra consideration in the discussion following.

Previous reports simply evaluate the non-detects at the detection limit, thereby providing average values that are the maximum possible exposures based on our data. Since one of the prime purposes behind WUATM is the collection of data for purposes of assessing potential air toxics problems, this approach is justifiable, as it provides a maximized value for toxicological evaluations. The improvement of detection limits, however, may lead to a positive bias in the early portion of the project, resulting in an apparently decreasing trend over time.

Another equally defensible assumption for the incorporation of non-detects into a data set involves evaluating the null values at  $\frac{1}{2}$  the detection limit. While this may underestimate some potential health risks, it will tend to reduce positive biases associated with decreasing detection limits across the lifetime of a particular project. If, however, actual observed values under the less stringent detection limits are generally higher than those observed when the detection limits were improved, evaluating results at  $\frac{1}{2}$  the detection limit may mask trends associated with the detected values.

A final way of evaluating non-detects incorporated into this report is simply removal of the non-detects from the data set. This provides a basis for comparing what was actually observed in the ambient air during each phase of the project, even though disregarding the non-detects will raise average values above the actual value. Comparisons were made to determine whether there is a significant difference between the different approaches, and to attempt resolution of which to use in a given situation.

Variation between sites was evaluated using a standard T test. In cases where it appears that the sites do have distinguishable data sets, site is included as a covariate in further analysis. Otherwise, the data is treated as a single set. Yearly data was analyzed for trends using the least squares difference method and ANOVA. No analysis of seasonal variation was made at this time, as previous analysis of this type (reported in GBUATM 95) revealed no significant differences. Evaluations are presented on a parameter basis.

Each section includes tables of values used in further analysis, box plots representing the data, and least squares evaluations where applicable.

## Arsenic

Overall and yearly results for arsenic in Green Bay are presented in the tables and figures below. This parameter has a significant number of non-detects, and separate evaluations were made as discussed above. These evaluations are reported in the tables and figures below. A T-test performed on the data sets incorporating non-detects at the detection limit and at ½ the detection limit provided the following results:  $t = 17.858$ , probability = 0.000: indicating the likelihood that they are statistically different. Insufficient data was available for t-tests comparing the detect-only data sets with the others.

It should be noted that the years listed in these tables and figures refer to the project year, which runs from June until July. It should also be noted that the high value from 1995 (11.56 ng/m<sup>3</sup>) was invalidated due to it's being analyzed under a different protocol (ICAP as opposed to AA). The AA analysis of the same sample yielded results of 1.24 ng/m<sup>3</sup>.

Each method of incorporating non-detects is tabulated and graphed below. The distribution of samples above the original detection limits are included in the third table. It is interesting to note that only 36 samples (13.9%) exceed the original detection limits.

**Table 22: Arsenic Evaluated at Detection Limits (ng/m<sup>3</sup>, unless noted)**

Statistical Values	Overall	1992	1993	1994	1995	1996	1997
Mean	1.59	1.97	1.76	1.78	1.32	1.14	1.18
Standard Error	0.03	0.06	0.02	0.03	0.08	0.08	0.20
Median	1.73	1.83	1.74	1.78	1.23	1.02	1.08
Standard Deviation	0.55	0.48	0.13	0.22	0.50	0.59	0.67
Relative Standard Dev (%)	34.4%	24.3%	7.3%	12.3%	37.9%	51.8%	56.8%
Minimum	0.54	1.65	1.56	0.61	0.54	0.55	0.54
Maximum	4.24	4.24	2.25	2.53	2.53	2.87	2.50
Detects (Count)	109	9	3	7	41	41	8
Samples (Count)	259	58	38	55	44	53	11
Detection Rate (%)	42.1%	15.5%	7.9%	12.7%	93.2%	77.4%	72.7%
Completion (%)	86.3%	96.7%	63.3%	91.7%	73.3%	88.3%	91.7%

**Table 23: Arsenic Evaluated at ½ Detection Limit (ng/m<sup>3</sup>, unless noted)**

Statistical Values	Overall	1992	1993	1994	1995	1996	1997
Mean	1.11	1.20	0.96	1.01	1.25	1.08	1.10
Standard Error	0.04	0.10	0.05	0.05	0.08	0.09	0.23
Median	0.91	0.91	0.88	0.89	1.21	1.02	1.08
Standard Deviation	0.58	0.75	0.33	0.39	0.52	0.66	0.76
Relative Standard Dev (%)	52.7%	62.8%	34.7%	38.8%	41.2%	61.5%	68.7%
Minimum	0.27	0.83	0.78	0.61	0.52	0.28	0.27
Maximum	4.24	4.24	2.25	2.53	2.53	2.87	2.50

**Table 24: Arsenic Detected Values Only** (ng/m<sup>3</sup>, unless noted)

<b>Statistical Values</b>	<b>Overall</b>	<b>1992</b>	<b>1993</b>	<b>1994</b>	<b>1995</b>	<b>1996</b>	<b>1997</b>
<b>Mean</b>	1.49	2.79	2.08	1.87	1.30	1.29	1.40
<b>Standard Error</b>	0.07	0.27	0.12	0.23	0.08	0.09	0.23
<b>Median</b>	1.23	2.56	2.15	1.95	1.22	1.16	1.11
<b>Standard Deviation</b>	0.72	0.82	0.21	0.62	0.51	0.59	0.66
<b>Relative Standard Dev (%)</b>	48.2%	29.3%	10.0%	33.0%	38.9%	45.8%	46.8%
<b>Minimum</b>	0.54	1.87	1.85	0.61	0.54	0.55	0.80
<b>Maximum</b>	4.24	4.24	2.25	2.53	2.53	2.87	2.50
<b>All Detects (Count)</b>	109	9	3	7	41	41	8
<b>Original Detection Limit (Count)</b>	36	9	3	6	6	10	2

The graphs on the following page present this data visually. Examination of these graphs indicates that there may be a decreasing trend over time. At the least, one can observe that the actual detected values have tended to decrease slightly across the years, even though the number of detected samples has increased significantly. ANOVA was used to indicate whether there may be trends that can be determined from this data.

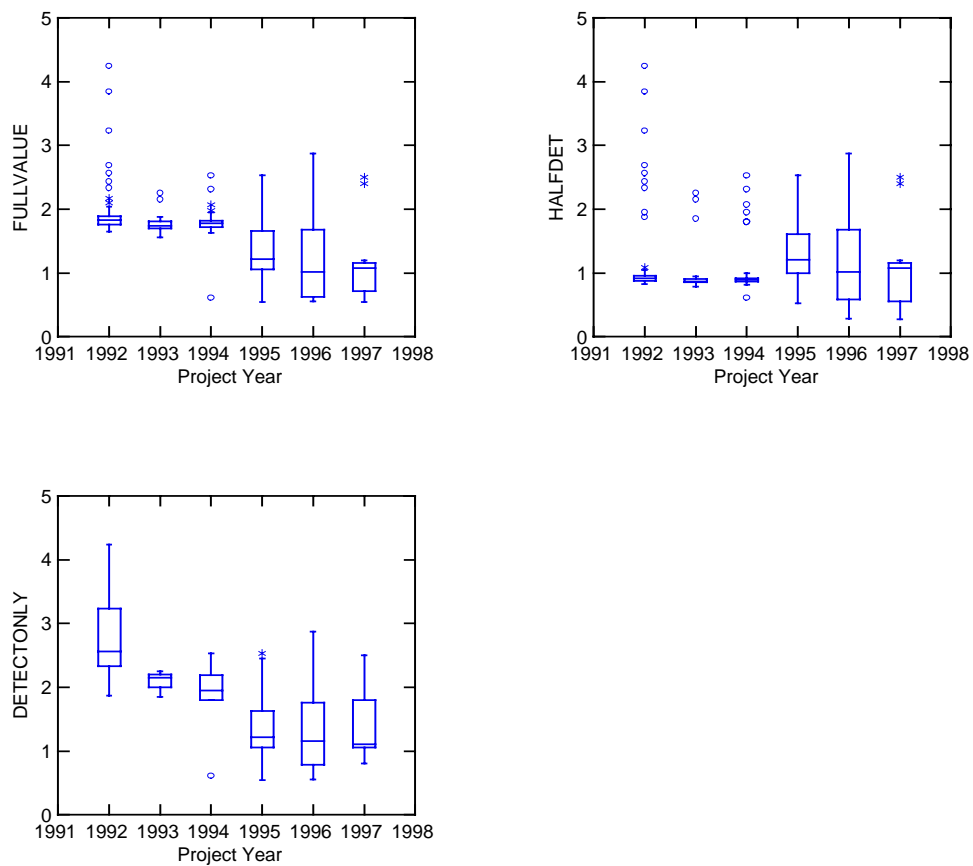
Analysis of the variation across years of the data sets shows significant differences in the data set evaluated at the detection limit (F-ratio = 27.753, P = 0.000). Somewhat significant differences are present in the detect-only data set (F-ratio = 12.075, P = 0.000); but no significant differences when the data is evaluated at ½ detection limits (F-ratio = 1.662, P = 0.144). The combination of these three results seems to support the tentative conclusion that there may be a slight decreasing trend over time, yet clearly shows that the low detection rate during the early portion of the project strongly affects the reliability of our data in determining trends. Least squares graphs are included following.

Differences between sites have been investigated in the same manner, using standard t-tests to determine whether the data sets are distinguishable from each other. Once again, this evaluation shows that the sites are distinguishable statistically when the non-detects are evaluated at the detection limit (t = 5.216, df = 206.1, Prob = 0.000), or excluded from the data set (t = 2.770, df = 31.6, Prob = 0.009). There is no significant difference if the non-detects are evaluated at ½ the detection limit (t = 1.203, df = 158.6, Prob = 0.231).

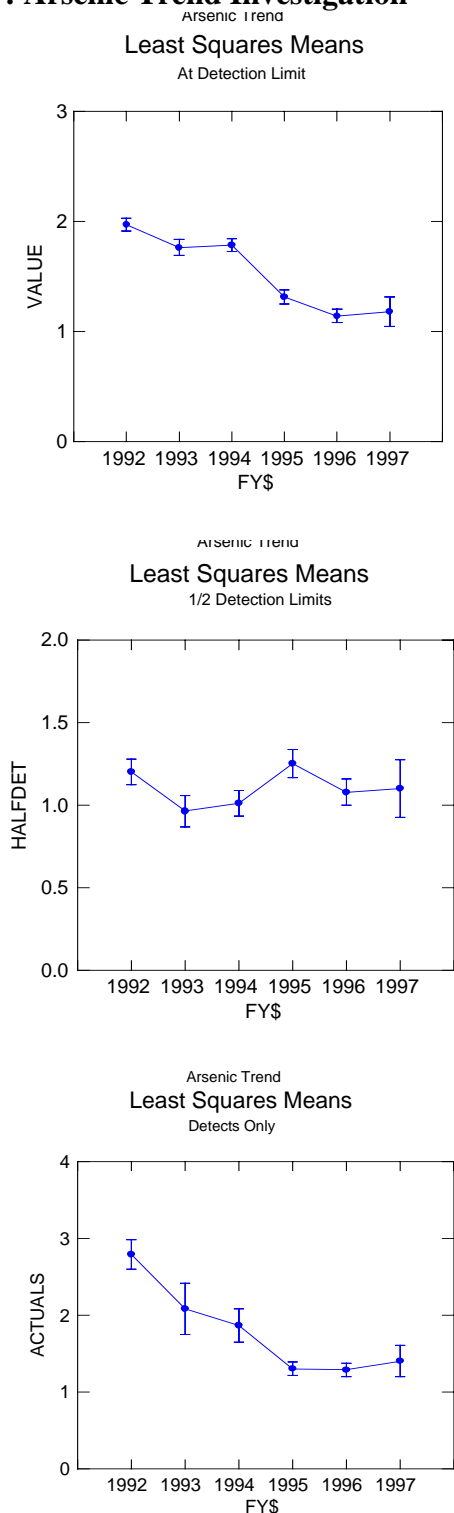
This case illustrates the difficulties surrounding evaluation of trends with data containing significant levels of non-detects. It appears safe to say that, on average, detected values from the early portion of the project were higher than detected values later on, but there is no clear way to distinguish between the effect of moving the site and the effect of any potential trends.

**Figure 6: Arsenic Results at Detection Limit,  $\frac{1}{2}$  Detection Limit, and Detects Only**

## Green Bay Arsenic Results



**Figure 7: Arsenic Trend Investigation**



The first and third of these graphs illustrate the apparently decreasing trend over time, while the middle one clearly shows little change.

It is interesting to note that reported emissions decreased by a factor of 4 between calendar years 1990 and 1992, after which they remained relatively constant. This trend may or may not represent a true decrease in the quantity of anthropogenic arsenic released to the atmosphere, because of the various factors discussed with the reported emissions section above.

That even such a slightly statistically valid trend is observed in our data in spite of the difficulties surrounding interpretation of non-detects indicates that our data may be appropriate for trend analysis, as per our purpose statement. As the data continues to improve over time (such as better detection limits), it's usefulness will continue to increase.



## Cadmium

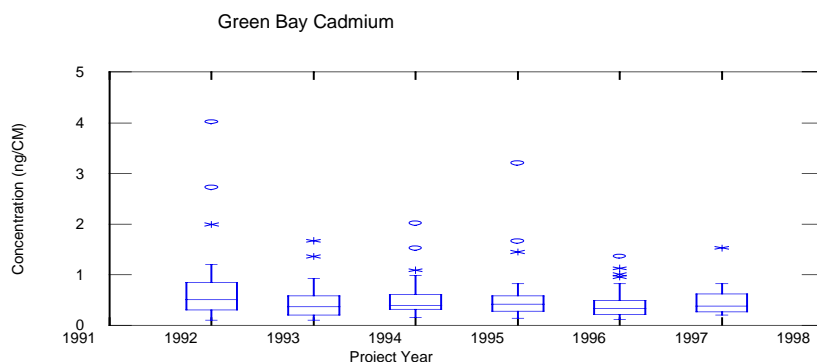
The overall detection rate for Cadmium was greater than 98% across all years of the project in Green Bay so that a t-test comparison of evaluations at the detection limit and at half detection shows no difference between the two data sets. Averaging observed values by site show that there is no difference between the two sites (0.600 ng/m<sup>3</sup> at Bay Beach, and 0.599 ng/m<sup>3</sup> at the Fox River station). ANOVA of the data grouped by years yields an F-ratio of 0.804, implying that there is not a significant trend observable. No least squares plot is included. Reported emissions decreased substantially after 1992, and have since been relatively insignificant in Brown County.

It should be noted that a single value above 5 ng/m<sup>3</sup> has been observed throughout the entire monitoring period (20.17 ng/m<sup>3</sup> in 1996), and a total of only 22 values greater than 1 ng/m<sup>3</sup>. Although this tends to cast some doubt on the high value, there has been no reason found to exclude this value from the data set. The high value has been excluded from the graph because of its effect on the scale.

**Table 25: Green Bay Cadmium Values, at Detection Limits** (ng/m<sup>3</sup> unless noted)

Statistical Values	Overall	1992	1993	1994	1995	1996	1997
Mean	0.60	0.67	0.45	0.51	0.53	0.80	0.52
Standard Error	0.08	0.08	0.06	0.04	0.08	0.38	0.12
Median	0.41	0.51	0.37	0.40	0.42	0.34	0.38
Standard Deviation	1.30	0.63	0.34	0.33	0.50	2.75	0.39
Relative Standard Dev (%)	217.0%	93.7%	76.6%	64.8%	95.1%	345.4%	74.2%
Minimum	0.11	0.11	0.11	0.16	0.14	0.12	0.21
Maximum	20.17	4.01	1.67	2.01	3.20	20.17	1.53
Detects (count)	255	57	35	55	45	52	11
Samples (count)	259	58	38	55	45	52	11
Detection Rate (%)	98.5%	98.3%	92.1%	100.0%	100.0%	100.0%	100.0%
Completion (%)	86.3%	96.7%	63.3%	91.7%	75.0%	86.7%	91.7%

**Figure 8: Green Bay Cadmium Results at Detection Limit**



## Chromium

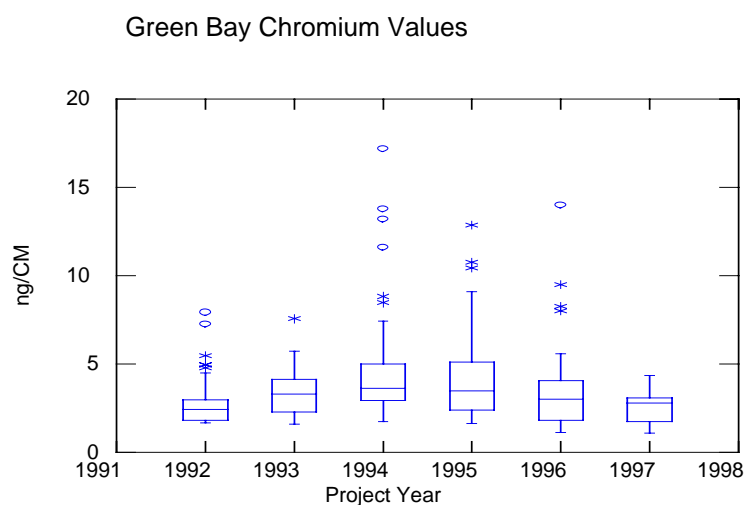
Chromium was detected in 88.8% of the samples across the sampling period, with most years being greater than 90%. For unknown reasons, the first year of the project has a significantly lower number of detects. A t-test comparing results from the two sites yields a t-value of 4.098, with a probability of 0.000 that the data set from the Fox River site is different from the Bay Beach site.

ANOVA was performed across the project years, both with no co-variate and with site as the co-variate. F- ratios from these analyses are 5.169 and 2.846, respectively, with resultant probabilities of 0.000 and 0.016, indicating the presence of statistical differences across the years. Examination of these trends is included on the following page.

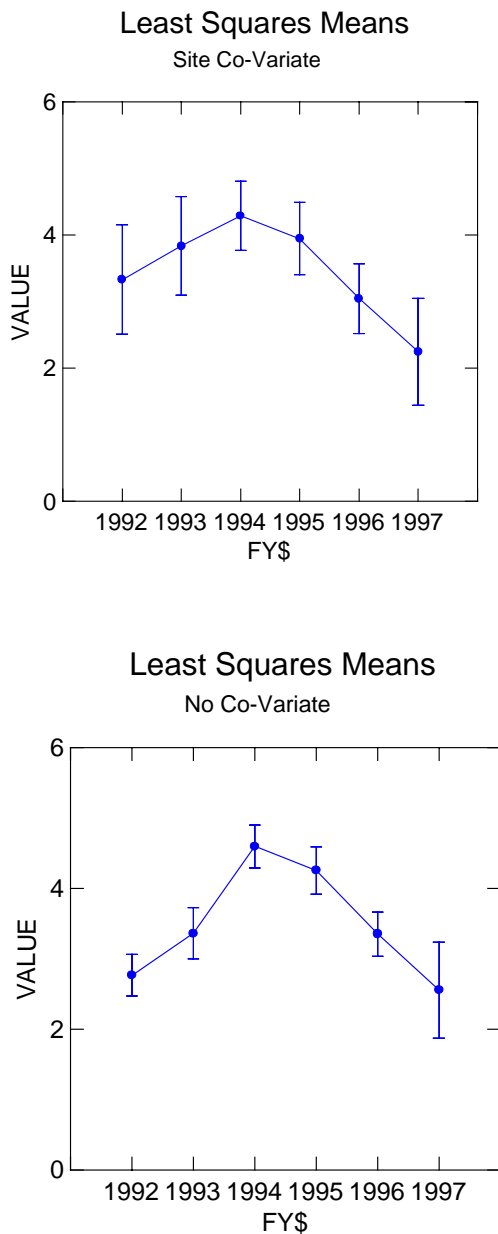
**Table 26: Green Bay Chromium Values, at Detection Limits (ng/m<sup>3</sup>, unless noted)**

Statistical Values	Overall	1992	1993	1994	1995	1996	1997
Mean	3.61	2.77	3.36	4.60	4.26	3.36	2.56
Standard Error	0.15	0.17	0.21	0.42	0.40	0.32	0.29
Median	2.98	2.41	3.28	3.60	3.47	3.00	2.77
Standard Deviation	2.35	1.32	1.30	3.12	2.67	2.34	0.97
Relative Standard Dev (%)	65.0%	47.7%	38.6%	67.8%	62.7%	69.8%	38.0%
Minimum	1.07	1.65	1.58	1.72	1.62	1.10	1.07
Maximum	17.15	7.90	7.55	17.15	12.85	13.98	4.34
Detects (count)	230	38	35	52	45	49	11
Samples (count)	259	58	38	55	45	52	11
Detection Rate (%)	88.8%	65.5%	92.1%	94.5%	100.0%	94.2%	100.0%
Completion (%)	86.3%	96.7%	63.3%	91.7%	75.0%	86.7%	91.7%

**Figure 9: Green Bay Chromium Values, at Detection Limit**



**Figure 10: Chromium Trend Analysis**



This potential trend is interesting in that the ambient chromium concentrations appear to increase through 1994, and then decrease. Statistically significant differences, however, exist only between both 1994 and 1995, and 1997 when site is included as a co-variate. Without site as a co-variate, 1992 and 1993 are also significantly different than 1994 and 1995.

A total of 8 values have been observed in excess of 10 ng/m<sup>3</sup>, of which 4 occur in 1994, 3 in 1995 and 1 in 1996. The presence of these values in the data set impacts the trend analysis.

Reported emissions of chromium compounds decreased significantly in 1992, after which values have remained essentially constant, so that this factor does not appear to play a role in the trends observed.

A potentially significant difference between the sites is that the Fox River site was located in a parking lot. Auto exhaust is a potential source of this element. Chromium is frequently alloyed in engine steels and can be emitted as the cylinder walls wear.

## Lead

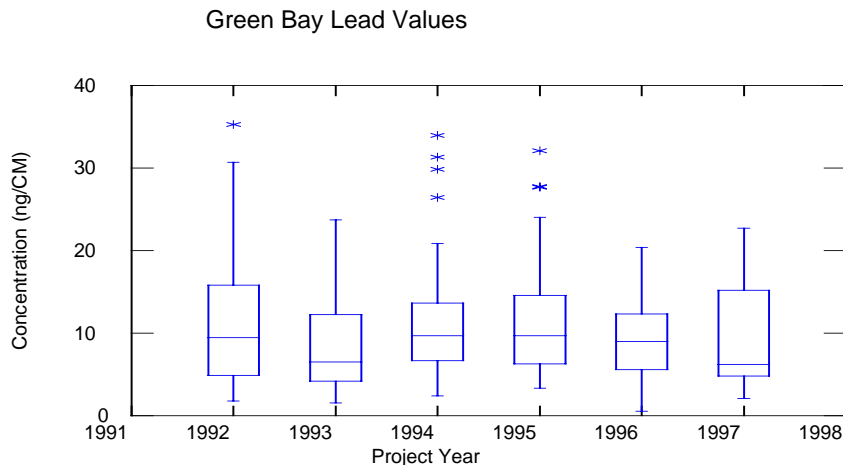
The detection rate for lead has been greater than 90% across all years of the project, so that there is not a statistical difference between evaluation of the non detects at the detection limit or at ½ the detection limit. Examination of the potential difference between the sites with a standard t test yields the values  $t = 1.159$  and  $\text{Prob} = 0.248$ , indicating that the two sites can not be distinguished from each other. Application of ANOVA across the project years yields an F-ratio of 0.503, indicating that the separate years of the project are not distinguishable. No least squares plot has been included. Reported emissions of lead are generally low in Brown County.

**Table 27: Green Bay Lead Values at Detection Limits** (ng/m<sup>3</sup>, except when noted)

Statistical Values	Overall	1992	1993	1994	1995	1996	1997
Mean	11.61	11.24	8.75	12.68	11.66	13.32	9.77
Standard Error	0.93	1.02	0.98	1.57	1.05	4.02	2.13
Median	9.22	9.51	6.56	9.74	9.73	9.45	6.20
Standard Deviation	15.02	7.77	6.07	11.63	7.02	28.98	7.05
Relative Standard Dev (%)	129.4%	69.1%	69.4%	91.7%	60.2%	217.5%	72.2%
Minimum	0.58	1.77	1.58	2.45	3.36	0.58	2.15
Maximum	215.76	35.34	23.75	81.43	32.12	215.76	22.78
Detects (count)	253	56	35	55	45	51	11
Samples (count)	259	58	38	55	45	52	11
Detection Rate (%)	97.7%	96.6%	92.1%	100.0%	100.0%	98.1%	100.0%
Completion (%)	86.3%	96.7%	63.3%	91.7%	75.0%	86.7%	91.7%

The two highest values for this parameter (81.43 ng/m<sup>3</sup> and 215.76 ng/m<sup>3</sup>) have been excluded from the graph to prevent scaling difficulties.

**Figure 11: Green Bay Lead Values, at Detection Limits**



## Selenium

Improvements in the analytical detection limit for Selenium led to a significant increase in the detection rate for this parameter. A t-test performed comparing results evaluating non-detects at the detection limit and at ½ the detection limit yielded a t value of 17.493 and a probability of 0.000. Evaluations of results at the detection limit, ½ the detection limit and with the detected values only are included in the table and graphs following. The distribution of values greater than the original detection limit is included in the third table.

**Table 28: Selenium Results at Detection Limit** (ng/m<sup>3</sup>, unless otherwise noted)

Statistical Values	Overall	1992	1993	1994	1995	1996	1997
Mean	1.70	1.96	1.91	1.91	1.74	1.11	1.18
Standard Error	0.04	0.07	0.08	0.06	0.13	0.10	0.23
Median	1.75	1.82	1.76	1.79	1.59	0.67	0.65
Mode	1.70	1.85	1.71	1.72	1.22	0.60	0.54
Standard Deviation	0.71	0.51	0.50	0.46	0.89	0.71	0.75
Relative Standard Dev (%)	41.7%	25.9%	26.0%	23.9%	50.9%	63.8%	64.0%
Minimum	0.49	1.60	1.56	0.61	0.53	0.49	0.54
Maximum	4.51	4.14	4.30	3.39	4.51	2.81	2.57
Detects (count)	106	9	9	15	38	29	6
Samples (count)	259	58	38	55	45	52	11
Detection Rate (%)	40.9%	15.5%	23.7%	27.3%	84.4%	55.8%	54.5%
Completion (%)	86.3%	96.7%	63.3%	91.7%	75.0%	86.7%	91.7%

**Table 29: Selenium Results at ½ Detection Limit** (ng/m<sup>3</sup>, unless otherwise noted)

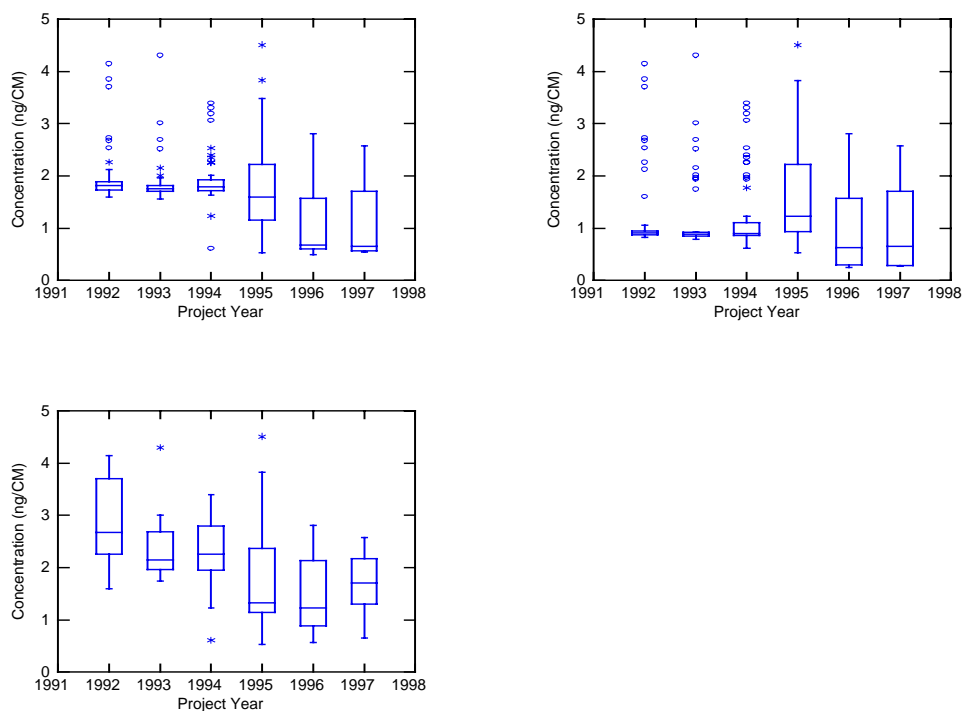
Statistical Values	Overall	1992	1993	1994	1995	1996	1997
Mean	1.24	1.20	1.25	1.27	1.60	0.98	1.05
Standard Error	0.05	0.10	0.13	0.10	0.14	0.11	0.26
Median	0.91	0.91	0.89	0.90	1.23	0.63	0.65
Standard Deviation	0.83	0.78	0.79	0.74	0.94	0.82	0.87
Relative Standard Dev (%)	66.8%	65.1%	63.2%	58.4%	58.5%	83.2%	83.3%
Minimum	0.25	0.82	0.78	0.61	0.53	0.25	0.27
Maximum	4.51	4.14	4.30	3.39	4.51	2.81	2.57
Detects (count)	106	9	9	15	38	29	6
Samples (count)	259	58	38	55	45	52	11
Detection Rate (%)	40.9%	15.5%	23.7%	27.3%	84.4%	55.8%	54.5%
Completion (%)	86.3%	96.7%	63.3%	91.7%	75.0%	86.7%	91.7%

**Table 30: Detected Selenium Values** (ng/m<sup>3</sup>, unless otherwise noted)

Statistical Values	Overall	1992	1993	1994	1995	1996	1997
Mean	1.91	2.84	2.48	2.28	1.73	1.52	1.69
Standard Error	0.09	0.29	0.27	0.20	0.16	0.13	0.27
Median	1.92	2.67	2.15	2.26	1.33	1.23	1.71
Standard Deviation	0.92	0.86	0.80	0.77	0.96	0.73	0.67
Relative Standard Dev (%)	48.4%	30.4%	32.2%	33.6%	55.6%	47.8%	39.8%
Minimum	0.53	1.60	1.74	0.61	0.53	0.57	0.65
Maximum	4.51	4.14	4.30	3.39	4.51	2.81	2.57
Samples (count)	106	9	9	15	38	29	6
Original Limit Detects	64	9	9	13	15	13	4

**Figure 12: Selenium Values, At Detection Limit, ½ Detection Limit, and Detects Only**

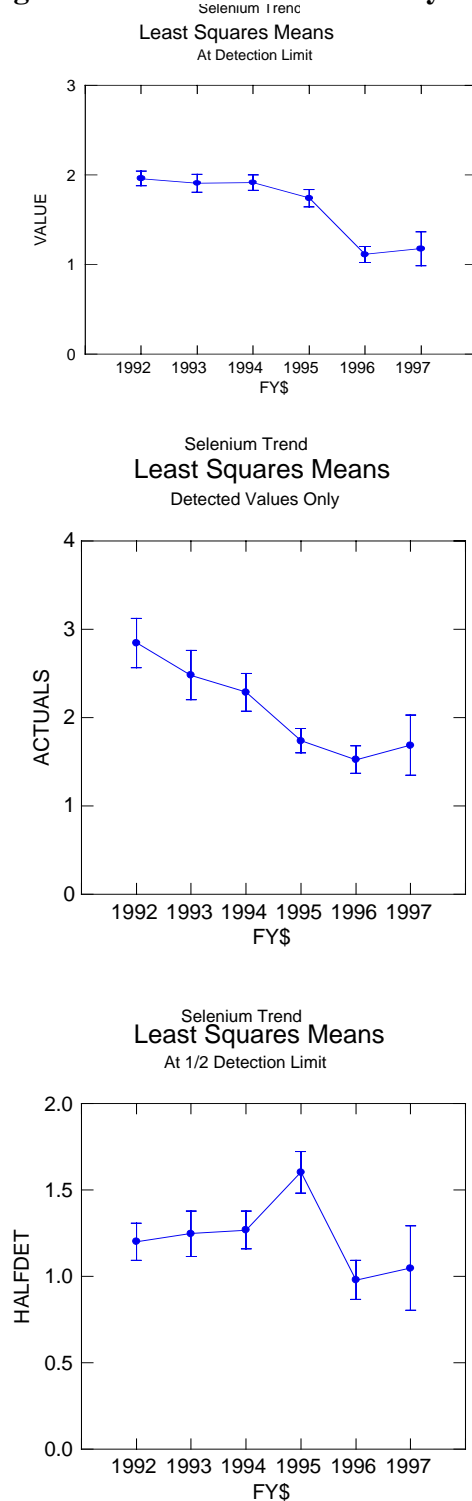
### Green Bay Selenium Values



Examination of the values on a per site basis yields a t value of 4.814 and a probability of 0.000 when results are evaluated at the detection limit, and a t value of 0.094 with a probability of 0.925 using  $\frac{1}{2}$  the detection limit. Evaluation using only the detected values yields a t value of 4.198 and a probability of 0.000. Once again, as with arsenic, the presence of a significant percentage of non-detects makes true distinctions between the sites difficult to discern, and readily confused with the effect of improving the detection limits.

Trend analysis across the years of the project using ANOVA techniques yields an F-ratio of 14.593 with a probability of 0.000 using the detection limit determinations. This analysis shows 1996 and 1997 to be significantly less than the rest of the years (probability values of less than 0.008). An F-ratio of 3.009 and probability of 0.012 are obtained when the ANOVA is performed using the  $\frac{1}{2}$  detection limit values, with 1995 being significantly larger than the rest of the years. Meanwhile, the actual detected values yield ANOVA values of 5.301 and 0.000, respectively, with 1995 and 1996 being significantly less than 1992 (probability = 0.009 and 0.000, respectively). Least square means graphs of these three conflicting trends are included below.

**Figure 13: Selenium Trend Analysis**



These graphs illustrate the difficulties of analyzing trends from our data as it stands. The most pertinent observation is that the detected values appear to decrease over time (middle graph), although only two years (1995 and 1996) differ statistically from any others (1992 only).

The fact that evaluation at  $\frac{1}{2}$  the detection limit shows 1995 to be statistically higher than any of the other years appears to be related to the detection rate that year, which, at 84.4%, is greater than that for any other year. Thus fewer of the values were affected by the detection limit factor.

Overall, a weak decreasing trend appears to be present, which appears to be validated when one observes that the most recent years' detection rates have decreased to about 55%, in spite of the improvement in detection limits.

With this information in mind it is interesting to note that the year with the highest reported selenium emissions in Brown County is 1995, in which 4 - 8 times as many emissions are reported as any other year.



## Vanadium

This parameter is the least detected metal through out the course of the project (overall detection rate of 22.4%). No detects were recorded during the first two years of the project. In 1994 there was a 5-fold improvement in detection limits. A total of 5 samples were reported at values greater than the original detection limit, all in 1994 and 1995.

These factors cast major doubts on the validity of trend analysis, and inter-site comparisons. As such, these evaluations are not performed. Results are summarized with all three evaluations of non-detects.

**Table 31: Vanadium Results at Detection Limit (ng/m<sup>3</sup>, unless otherwise noted)**

Statistical Values	Overall	1992	1993	1994	1995	1996	1997
Mean	4.19	6.04	5.80	5.95	1.90	1.63	1.57
Standard Error	0.16	0.05	0.04	0.35	0.19	0.11	0.16
Median	5.65	6.02	5.80	5.89	1.23	1.26	1.40
Standard Deviation	2.49	0.38	0.25	2.61	1.27	0.78	0.54
Relative Standard Dev (%)	59.5%	6.3%	4.3%	43.9%	67.1%	47.8%	34.7%
Minimum	1.03	5.34	5.19	1.23	1.08	1.10	1.03
Maximum	23.30	7.23	6.25	23.30	6.27	4.39	2.71
Detects (Count)	58	0	0	5	18	27	8
Samples (Count)	259	58	38	55	45	52	11
Detection Rate (%)	22.4%	0.0%	0.0%	9.1%	40.0%	51.9%	72.7%
Completion (%)	86.3%	96.7%	63.3%	91.7%	75.0%	86.7%	91.7%

**Table 32: Vanadium Results at ½ Detection Limit (ng/m<sup>3</sup>, unless otherwise noted)**

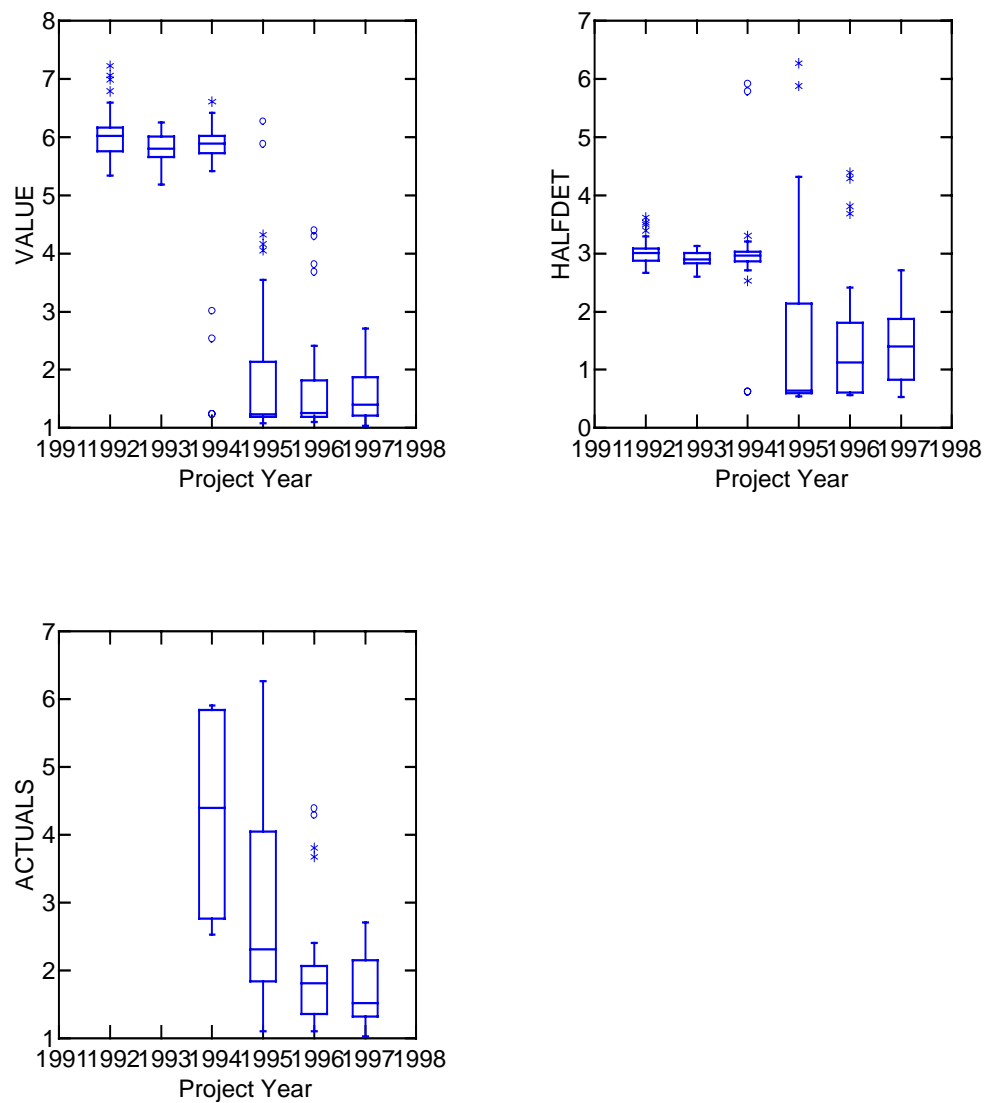
Statistical Values	Overall	1992	1993	1994	1995	1996	1997
Mean	2.41	3.02	2.90	3.35	1.54	1.34	1.41
Standard Error	0.11	0.03	0.02	0.38	0.22	0.14	0.21
Median	2.85	3.01	2.90	2.97	0.64	1.13	1.40
Standard Deviation	1.73	0.19	0.13	2.84	1.49	0.97	0.71
Relative Standard Dev (%)	71.8%	6.3%	4.3%	84.8%	97.0%	72.7%	50.7%
Minimum	0.54	2.67	2.60	0.62	0.54	0.56	0.54
Maximum	23.30	3.62	3.13	23.30	6.27	4.39	2.71
Detects (count)	58	0	0	5	18	27	8
Samples (count)	259	58	38	55	45	52	11
Detection Rate (%)	22.4%	0.0%	0.0%	9.1%	40.0%	51.9%	72.7%

**Table 33: Detected Vanadium Values (ng/m<sup>3</sup>, unless otherwise noted)**

Statistical Values	Overall	1994	1995	1996	1997
Mean	2.78	8.11	2.94	2.01	1.72
Standard Error	0.40	3.86	0.36	0.18	0.20
Median	1.87	5.78	2.32	1.81	1.53
Standard Deviation	3.05	8.63	1.51	0.94	0.57
Relative Standard Dev (%)	109.4%	106.5%	51.5%	46.5%	33.2%
Minimum	1.03	2.53	1.11	1.10	1.03
Maximum	23.30	23.30	6.27	4.39	2.71
Detects (count)	58	5	18	27	8
Original Limit Detects (count)	5	3	2		

**Figure 14: Vanadium Values at Detection Limit,  $\frac{1}{2}$  Detection Limit, and Detects Only**

## Green Bay Vanadium Values



## ***Inorganic Parameter Conclusions***

Analysis of the Green Bay and statewide metals sampling and analysis programs yields the following pertinent points of interest:

1. Expansion of the sampling program from a single site to five sites with a corresponding decrease in sampling frequency has not materially affected the representativeness of the data.
2. The statewide metals sampling program operates at a lowered confidence level because of the decrease in sampling frequency.
3. Statistically significant differences between the different sites chosen for the statewide program are observable in spite of the lowered confidence level.
4. Comparison of the urban sites to Trout Lake indicates the potential of determining urban impact with respect to these parameters. This potential will be investigated further in the future, as more data is collected.
5. Historic Green Bay data clearly demonstrates the impact improving detection limits can have on data sets that contain significant quantities of non-detects.
6. Slight decreasing trends are observed with respect to Arsenic and Selenium values in Green Bay.
7. Chromium displays an increasing trend through 1994, and then decreases afterwards.
8. Cadmium and Lead values remain essentially constant throughout the testing period in Green Bay.
9. Vanadium trends are not discernible because of the low overall detection rate throughout the course of the project.
10. Emission reporting may not be a valid indicator of actual emissions, and may demonstrate trends that are not observable in the ambient data collected.

## **Carbonyl Parameters**

### ***Overview***

The primary carbonyl parameter in the WUATM study is formaldehyde, with some data present for acetaldehyde, acetone and occasional detects of acrolein and others. Consistent data on parameters other than formaldehyde has not been obtained. All 1997 WUATM project year data is presented in this report.

An analysis of 24-hour formaldehyde results collected during the entire WUATM project in Green Bay is presented for project closure. This data is compared with 24 hour sample results from the Photochemical Assessment Monitoring (PAMS) program collected at the University of Wisconsin - Milwaukee, North Campus (UWM: AIRS#55-079-0041) between April 1992 and June 1997.

Previous WUATM reports have concentrated on the Green Bay sites, without presenting data collected as part of the PAMS program. All PAMS related data has been previously reported in the PAMS data reports. Additional samples have been collected on a 3 hour basis at UWM and two additional sites along Lake Michigan (Harrington Beach State Park and Manitowoc). These results are not included, as they are not directly comparable to the existing WUATM data set.

Background information on the uses, atmospheric sources and reported emissions in Wisconsin are included along with the data. This data is presented in several sections. The first section deals with the results and quality control summary of the Green Bay monitoring data between July 1996 and June 1997. This is followed by summaries of historic UWM and Green Bay results (completeness and quality control parameters are not included). The final section presents an analysis of all the data, including seasonal and yearly trend analysis, and inter-site comparisons.

### ***Parameter Uses and Atmospheric Sources***

Formaldehyde is a highly reactive, colorless organic gas with a pungent odor. It is widely present in the atmosphere at low concentrations, through both a myriad of consumer and industrial uses, and as a product of incomplete combustion. Indirect production through photochemical oxidation of hydrocarbons released from combustion processes may be greater than direct production at times.

Natural mechanisms for formaldehyde removal include dissolution in water, where it breaks down readily through biological processes, direct photolysis and oxidation by photo-chemically produced species in the air. The compound is very short lived, with some half-life estimates ranging from 1.6 to 19 hours, dependent upon atmospheric conditions.

Complete oxidation of formaldehyde yields carbon dioxide and water, however it tends to form intermediates known as free radicals that participate in further atmospheric reactions. The compound has been implicated in the ozone formation and degradation cycles, and is included in

the PAMS monitoring program for this reason.

Uses of formaldehyde include being an intermediate in the industrial production of organic chemicals; production of urea-formaldehyde resins which are used in plywood glues; particle board products and insulating foams; disinfecting and preservative products; slow release fertilizers; and as an anti-bacterial agent in many cosmetic and disinfectant products.

The wide variety of consumer product uses and volatile nature of the material lead to a situation where it is common for indoor concentrations of formaldehyde to be much greater than those typically found outdoors. This is especially true in newer and mobile homes, where out-gassing from construction materials is typical. As the materials age, out-gassing decreases, and concentrations gradually lower.

Emissions of biogenic compounds from natural sources also fuel the formation of atmospheric formaldehyde, through essentially the same reaction pathways that products of incomplete production follow. Elevated concentrations in remote sites are frequently associated with long range transport of reactive organic compounds, rather than local, direct sources of formaldehyde.

### ***Reported Emissions***

Industrial sources which emit quantities of toxic materials above particular limits are required to report their emissions to the DNR. Reporting requirements have varied, and all potential sources may not be identified. The reported emissions are typically estimated based on process material throughput and standard emission factors which have been developed by the EPA. Significant variation among facilities operating similar equipment is common, and may not be reflected in the standard emission factors.

These factors render reported emissions data useful mostly as an order of magnitude estimate of industrial emissions. The significant quantities of formaldehyde emitted from non-industrial sources and formed in atmospheric reactions from anthropogenic pre-cursors are difficult to assess. As such, emissions reported in Table 35 must be regarded as a very rough guideline, rather than a true estimate of Wisconsin's atmospheric formaldehyde inputs.

Reported toxic releases both statewide, and in Brown and Milwaukee counties, between 1990 and 1997 are summarized in the table below. Emissions are in pounds per year. Two values from the original AEMS data have been altered. One source reported over 12,000,000 pounds emitted in 1992, while all other years reported are around 400. This value was deleted. Another source reported over 3,000,000 pounds emitted in 1991, while all other years on record are less than 1/10<sup>th</sup> that level and decreasing. The suspect value was divided by 10.

It should be noted that in general emissions appear to be decreasing since the advent of reporting in response to the Clean Air Act in 1990. Many major sources have improved either their pollution control, or their emission estimation assumptions, to reduce their annual output of this

pollutant. Combustion processes are a major source that can be minimized by better monitoring and control of boiler conditions. More efficient combustion implies lessened energy cost, which may help spur efforts to decrease atmospheric inputs.

It is also interesting to note that a significant number of sources report estimated emissions of less than a pound per year. This represents a value less than the average amount associated with an individual's personal production of formaldehyde related to use of gas fired appliances, personal vehicles and smoking. The minimum required reporting limit for this compound is 125 pounds per year.

**Table 35: Reported Industrial Emissions of Formaldehyde in Wisconsin,**

<b>Year</b>	<b>1990</b>	<b>1991</b>	<b>1992</b>	<b>1993</b>	<b>1994</b>	<b>1995</b>	<b>1996</b>	<b>1997</b>
<b>All Reporting Sources Statewide</b>								
<b>Emissions</b>	859628	850703	498486	431876	346650	288931	273567	302784
<b>Sources</b>	273	294	357	320	301	254	245	266
<b>Largest</b>	308246	310487	151921	100209	24334	29948	27042	41776
<b>Statewide Sources &gt;1000 Pounds per Year</b>								
<b>Emissions</b>	833395	814453	446317	380858	298264	241514	225380	254237
<b>% Emissions</b>	96.9%	95.7%	89.5%	88.2%	86.0%	83.6%	82.4%	84.0%
<b>Sources</b>	49	59	68	62	61	48	49	51
<b>% Sources</b>	17.9%	20.1%	19.0%	19.4%	20.3%	18.9%	20.0%	19.2%
<b>Statewide Sources &gt;10000 Pounds per Year</b>								
<b>Emissions</b>	719062	662421	262289	231456	124278	129412	94003	133974
<b>% Emissions</b>	83.6%	77.9%	52.6%	53.6%	35.9%	44.8%	34.4%	44.2%
<b>Sources</b>	12	14	10	11	7	7	5	7
<b>% Sources</b>	4.4%	4.8%	2.8%	3.4%	2.3%	2.8%	2.0%	2.6%
<b>Brown County Emissions</b>								
<b>Emissions</b>	4991.2	9400.3	12966.8	23584.0	18219.4	19327.5	13364.2	15819.1
<b>% Emissions</b>	0.6%	1.1%	2.6%	5.5%	5.3%	6.7%	4.9%	5.2%
<b>Sources</b>	8	8	17	13	14	13	12	14
<b>% Sources</b>	2.9%	2.7%	4.7%	4.1%	4.7%	5.1%	4.9%	5.3%
<b>Milwaukee County Emissions</b>								
<b>Emissions</b>	16508.0	14066.9	16496.2	14861.4	16421.9	7446.2	7653.9	12043.1
<b>% Emissions</b>	1.9%	1.7%	3.3%	3.4%	4.7%	2.6%	2.8%	4.0%
<b>Sources</b>	25	23	30	22	22	25	24	24
<b>% Sources</b>	9.2%	7.8%	8.4%	6.9%	7.3%	9.8%	9.8%	9.0%

## **Current WUATM Formaldehyde**

### **Data Completeness**

Previous protocols called for the collection of samples on a one in twelve day schedule, for a total of 30 samples per year from the Fox River Site. Attempts to expand the coverage of the toxics monitoring network without a concurrent increase in funding, and combined with a generally stable formaldehyde presence observed in the samples, led to the choice to decrease the sampling frequency for this parameter.

Sampling during the 1996 - 1997 project year was conducted on a one in thirty day schedule. With a single site, a total of 12 samples could have been analyzed. This choice has the side effect of reducing the certainty of our average observations and increasing the standard error. An evaluation of the representativeness of our current data set with the respect to historic data is included.

Project completeness with reference to formaldehyde is documented in table F2 below. Completeness is the ratio of valid ambient samples that were analyzed for formaldehyde, to total Sampling days. All samples had results returned, for an analytical completeness of 100%. Overall project completeness stands at 84.6%, with 132 samples returned from a total of 156 sample days.

**Table 36: WUATM Formaldehyde Completeness, Green Bay**

<b>Project Year</b>	<b>Completeness</b>	<b>Samples</b>	<b>Ambient</b>	<b>Blanks</b>	<b>Duplicates</b>	<b>Sampling Days</b>
1997	91.7%	16	11	0	5	12

### **Analytical Results**

Results of current carbonyl analysis are presented in the following table. It should be noted that this is the last sampling season wherein acetaldehyde and acetone results have been actively requested by the WUATM program. The reasons behind this are related to inconsistently variable results for acetone which appear to be a function of frequent lab or sampling contamination, and the relatively low toxicity of acetaldehyde. Although we request that random other parameters observed (such as propionaldehyde or acrolein) be reported when they appear to be significant, there were no other parameters reported by the lab this year.

Values reported are in  $\mu\text{g}/\text{m}^3$ . Averages, maxima, minima and %relative standard deviations are shown, along with the number of samples, the number of detects and the resulting % detection. Non-detects are valued at the detection limit in this section. This is the general convention used in the WUATM to generate maximum potential concentrations for the evaluation of health risks.

**Table 37: Current Green Bay Carbonyl Sampling Results ( $\mu\text{g}/\text{m}^3$ )**

Parameter Name	Average	Maximum	Minimum	%RSD	Samples	Detects	%Detection
Acetaldehyde	0.90	1.98	0.33	69.1%	14	14	100.0%
Acetone	4.07	28.15	1.04	173.0%	14	14	100.0%
Formaldehyde	0.48	1.04	0.05	74.8%	16	12	75.0%

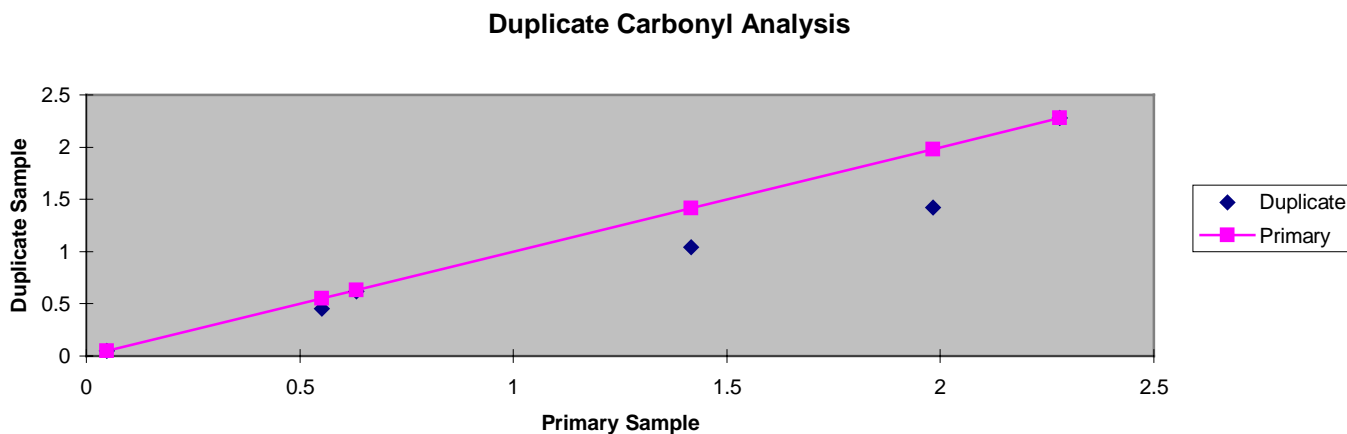
## Quality Assurance Parameters

Quality assurance samples obtained include 3 sets of duplicate samples, of which 2 are from co-located samplers. Duplicate analysis show a total of 9 data pairs, of which 3 (33.3%) have been invalidated (the first co-located pairs) because of apparent sampler problems. These results are included in the table for comparison, but the percent relative standard deviation (%RSD) is not included. The remaining 6 pairs are all within  $\pm 25\%$ , with an overall average of  $\pm 10.2\%$ , well within the QC goals of  $\pm 15\%$ . Formaldehyde duplicate precision averages 1.6%.

**Table 38: Duplicate Carbonyl Sample Values**

Duplicate Precision	Primary	Duplicate	Average	% RSD	Detects	
Acetaldehyde	0.38	0.42	0.40		Y/Y	1st Co-Located
Acetaldehyde	1.98	1.42	1.70	23.2%	Y/Y	2nd Co-Located
Acetaldehyde	0.55	0.46	0.50	13.3%	Y/Y	
Acetone	5.74	28.15	16.95		Y/Y	1st Co-Located
Acetone	1.42	1.04	1.23	21.4%	Y/Y	2nd Co-Located
Acetone	2.28	2.28	2.28	0.0%	Y/Y	
Formaldehyde	0.21	0.05	0.13		Y/N	1st Co-Located
Formaldehyde	0.63	0.62	0.62	1.8%	Y/Y	2nd Co-Located
Formaldehyde	0.05	0.05	0.05	1.4%	N/N	

**Figure 15: Comparison of Primary and Duplicate Analyses**





There were no blank samples submitted within the WUATM submitted this year, however a total of 7 valid blanks from the same lot were submitted for the PAMS program. Formaldehyde results from these samples are shown in the following table. There were no observed formaldehyde concentrations above reporting limits associated with the materials used in Milwaukee.

**Table 39: Blank Carbonyl Sample Results**

Sample Date	Formaldehyde	Acetaldehyde	Acetone
22-Oct-96	<0.050	<0.075	0.25
22-Oct-96	<0.050	0.13	0.37
20-Nov-96	<0.049	<0.073	0.34
24-Apr-96	<0.048	0.15	
29-Oct-96	<0.049	<0.073	0.25
30-Jan-97	ND<0.052	<=0.13	0.67
19-Apr-97	ND<0.060	ND<0.090	1.6

### **Data Representativeness**

A major concern with the current data is the representativeness of our data set with the decrease in sampling frequency. A t-test was performed comparing data collected under the previous 1 in 12 day schedule and the current 1/30 day schedule. The data was found to be statistically indistinguishable at the 95% confidence limit (probability of 0.081). Although this implies that there has been little to no effect on our data, it should be noted that the 1997 sampling season recorded the lowest average, minimum and maximum values of the program.

The presence of a very few samples with significantly higher concentrations, and the general variability at each site introduces the potential for a low level sampling strategy to yield very different results from a higher sample density program (such as PAMS), if the random high or low concentration events happened to be preferentially captured within the smaller sample set.

### ***Historic Green Bay and Milwaukee Formaldehyde Results***

A total of 145 samples from Green Bay and 272 - 24 hour samples from Milwaukee have been analyzed for formaldehyde during the course of the WUATM and PAMS sampling programs. All results are presented in the tables and graphs below. It should be noted that a small number of results greater than 10  $\mu\text{g}/\text{m}^3$  have been obtained from each site.

The high concentration samples from Green Bay are somewhat randomly scattered throughout the Fox River Site sample set. This site was located in a parking lot along the lower Fox River, and therefore subject to exhaust from both cars and shipping. High values were obtained across a four year period, and represent a variety of sample cartridge lots that have valid blanks and low concentration samples associated with them.

The pattern observed with the Milwaukee results is markedly different. All high values are observed in a two month period during the summer of 1994 (project years 94 and 95), during which all observed values are unusually high. Sample materials are from three different lots, none of which has a clear record of being blank tested in 1994. One of the three lots has a low concentration sample representative, while the others have only high values associated with them. Thus, contamination of the sampling materials or the site itself are definite possibilities.

Although no sure reason to disregard these high values has been found, the small number of samples in this category (less than 3.5% of samples) lends suspicion as to their validity. Results are summarized both on the basis of all samples, and all samples less than  $10 \mu\text{g}/\text{m}^3$ . Five tables below document formaldehyde results. These tables present the complete Green Bay and Milwaukee data sets, followed by the respective “low value” only sets. The final table documents the values above  $10 \mu\text{g}/\text{m}^3$  excluded from the truncated data set. Evaluation of both data sets allows for comparison of “typical” and “extreme” values

**Table 40: Historic WUATM Formaldehyde Results**

<b>Green Bay All Values</b>	<b>Overall</b>	<b>1992</b>	<b>1993</b>	<b>1994</b>	<b>1995</b>	<b>1996</b>	<b>1997</b>
Mean	2.11	0.84	2.62	3.41	4.45	1.62	0.47
Standard Error	0.61	0.29	1.90	1.86	3.29	0.51	0.09
Median	0.60	0.48	0.48	0.62	0.99	0.81	0.62
Standard Deviation	7.31	1.49	10.23	8.10	13.58	3.08	0.35
Rel. Standard Dev. (%)	345.8%	178.4%	390.0%	237.8%	305.4%	190.3%	74.1%
Range	57.02	7.90	55.58	33.51	56.62	18.34	0.99
Minimum	0.05	0.07	0.09	0.24	0.45	0.11	0.05
Maximum	57.06	7.97	55.67	33.75	57.06	18.45	1.04
Count	145	27	29	19	17	37	16
Confidence Level(95.0%)	1.20	0.59	3.89	3.91	6.98	1.03	0.19

**Table 41: Historic PAMS 24-Hour Formaldehyde Results**

<b>Milwaukee All Values</b>	<b>Overall</b>	<b>1992</b>	<b>1993</b>	<b>1994</b>	<b>1995</b>	<b>1996</b>	<b>1997</b>
Mean	2.74	1.94	1.65	3.86	4.15	2.19	2.37
Standard Error	0.18	0.16	0.15	0.86	0.55	0.16	0.17
Median	2.01	1.94	1.44	2.45	2.96	1.88	1.78
Standard Deviation	2.94	0.56	1.08	5.01	4.19	1.19	1.31
Rel. Standard Dev. (%)	107.3%	29.0%	65.7%	129.9%	101.0%	54.5%	55.4%
Range	23.10	1.85	7.23	23.07	19.81	5.69	5.51
Minimum	0.05	0.89	0.51	0.08	0.99	0.05	0.83
Maximum	23.15	2.74	7.74	23.15	20.79	5.75	6.34
Count	272	13	54	34	59	55	57
Confidence Level(95.0%)	0.35	0.34	0.30	1.75	1.09	0.32	0.35

**Table 42: WUATM Formaldehyde Results, Excluding Values >10 µg/m<sup>3</sup>**

<b>Green Bay, Low Values</b>	<b>Overall</b>	<b>1992</b>	<b>1993</b>	<b>1994</b>	<b>1995</b>	<b>1996</b>	<b>1997</b>
Mean	0.90	0.84	0.73	0.92	1.16	1.15	0.47
Standard Error	0.09	0.29	0.13	0.21	0.20	0.20	0.09
Median	0.56	0.48	0.48	0.53	0.97	0.79	0.62
Standard Deviation	1.05	1.49	0.71	0.87	0.80	1.21	0.35
Rel. Standard Dev. (%)	116.8%	178.4%	97.7%	94.8%	69.2%	105.1%	74.1%
Range	7.93	7.90	3.34	3.70	2.82	4.85	0.99
Minimum	0.05	0.07	0.09	0.24	0.45	0.11	0.05
Maximum	7.97	7.97	3.44	3.94	3.26	4.95	1.04
Count	140	27	28	17	16	36	16
Confidence Level(95.0%)	0.18	0.59	0.28	0.45	0.43	0.41	0.19

**Table 43: PAMS 24 Hour Formaldehyde Results, Excluding Values >10 µg/m<sup>3</sup>**

<b>Milwaukee Low Values</b>	<b>Overall</b>	<b>1992</b>	<b>1993</b>	<b>1994</b>	<b>1995</b>	<b>1996</b>	<b>1997</b>
Mean	2.28	1.94	1.65	2.37	2.93	2.19	2.37
Standard Error	0.07	0.16	0.15	0.17	0.14	0.16	0.17
Median	1.97	1.94	1.44	2.41	2.94	1.88	1.78
Standard Deviation	1.19	0.56	1.08	0.93	1.06	1.19	1.31
Rel. Standard Dev. (%)	52.2%	29.0%	65.7%	39.2%	36.0%	54.5%	55.4%
Range	7.69	1.85	7.23	4.45	4.90	5.69	5.51
Minimum	0.05	0.89	0.51	0.08	0.99	0.05	0.83
Maximum	7.74	2.74	7.74	4.52	5.89	5.75	6.34
Count	264	13	54	31	54	55	57
Confidence Level(95.0%)	0.14	0.34	0.30	0.34	0.29	0.32	0.35

**Table 44: Values Greater Than 10 µg/m<sup>3</sup>**

<b>Site</b>	<b>Date</b>	<b>µg/m<sup>3</sup></b>	<b>Site</b>	<b>Date</b>	<b>µg/m<sup>3</sup></b>
Milwaukee	07-Jun-94	23.15	Fox River	10-Nov-94	57.06
Milwaukee	13-Jul-94	20.79	Fox River	13-Apr-93	55.67
Milwaukee	06-Aug-94	18.27	Fox River	09-Dec-93	33.75
Milwaukee	19-Jun-94	17.72	Fox River	27-Feb-96	18.45
Milwaukee	13-Jun-94	16.85	Fox River	02-Jan-94	15.41
Milwaukee	01-Jul-94	16.31			
Milwaukee	25-Jul-94	15.73	<b>Percent of Milwaukee Samples</b>		2.9%
Milwaukee	19-Jul-94	15.11	<b>Percent of Green Bay Samples</b>		3.4%

The data sets presented in the tables above are shown graphically in figures 16 – 20. Exclusion of the high values leads to a much better resolution for the majority of samples. It is interesting to note that the extreme values observed in Green Bay are significantly higher than the Milwaukee extremes.

## Data Comparisons, Green Bay Values

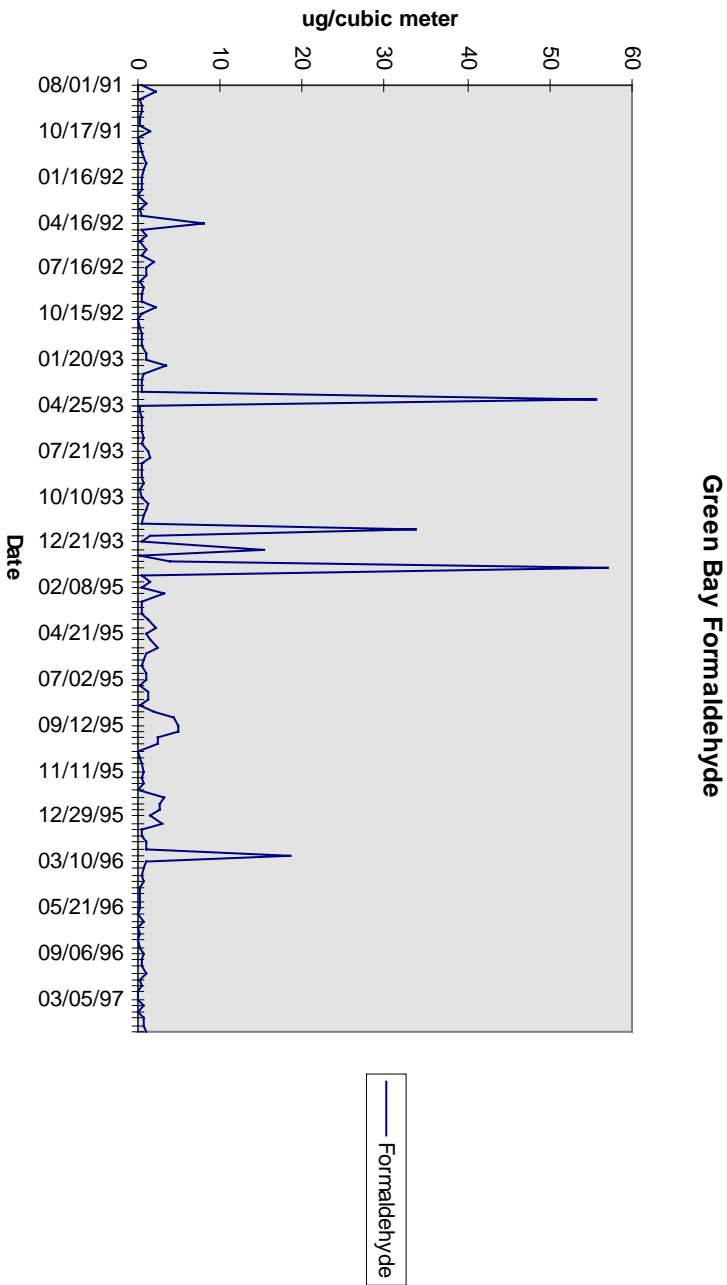
Evaluation of the data sets begins with a determination of whether there is a significant difference between the two sites used for the Green Bay WUATM project (Bay Beach and Fox River). T-tests performed on both sets of data yield no statistical difference between the sites ( $t = 1.454$ ,  $\text{prob} = 0.148$  for all values;  $t = 0.755$ ,  $\text{prob} = 0.451$  with high values excluded). As such, all further evaluations treat the Green Bay data as a single pool without including site as a co-variate.

Yearly and seasonal patterns were evaluated using ANOVA techniques, with the result that there is no statistical trend observable on either level. Yearly variance analysis yields F-ratios of 0.850 and 1.770 with probabilities of 0.517 and 0.123 using the entire and truncated data sets, respectively. Seasonal variance analysis yields F-ratios of 0.566 and 0.944, and probabilities of 0.638 and 0.421, respectively.

The final trend investigation with the Green Bay data is comparison with the Milwaukee data set. A t-test performed using the complete data sets indicates no statistically significant difference between the two sites ( $t = 1.237$ ,  $\text{prob} = 0.217$ ). Applying the same test to the truncated data sets, however, does yield a statistically significant difference ( $t = 11.513$ ,  $\text{Prob} = 0.000$ ). One potential interpretation of these results is that the “typical” average concentration of formaldehyde is higher in Milwaukee than it is in Green Bay, but random events tend to equalize overall background ambient urban exposures between the two cities.

It is important to note that indoor concentrations of formaldehyde are commonly found to exceed outdoor concentrations, so that an individual’s exposure to this compound is typically driven by factors outside of the scope of the WUATM and PAMS monitoring programs. All results from both sites below  $10 \mu\text{g}/\text{m}^3$  are shown in the following graphs, which clearly shows the differences between the cities. The first graph displays all values ordered by sample date, which shows the consistent nature of the differences between the cities. The second figure shows the distribution of samples as frequency histograms. Note that the program automatically places the data with the highest value data set on the left, so that the sites switch sides between the two plots.

**Figure 16: WUATM Ambient Formaldehyde Results, All Values**



**Figure 17: WUATM Ambient Formaldehyde Results, Values below 10  $\mu\text{g}/\text{m}^3$**

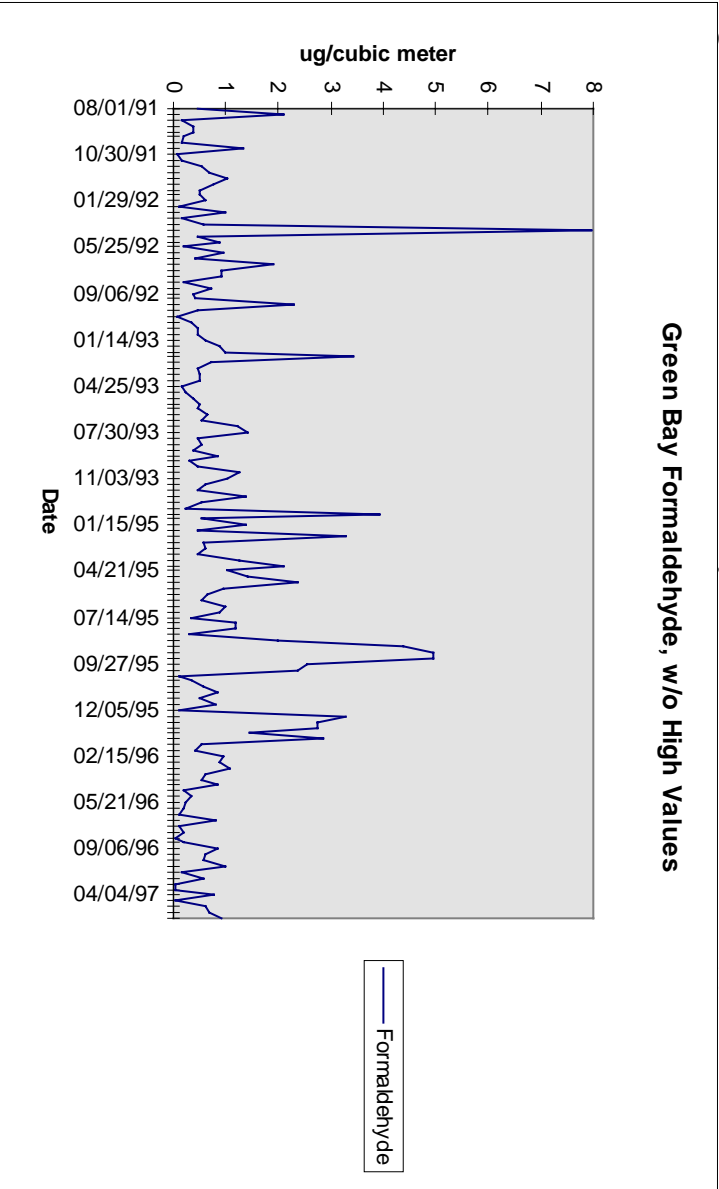


Figure 18: PAMS 24-Hour Formaldehyde Results, All Values

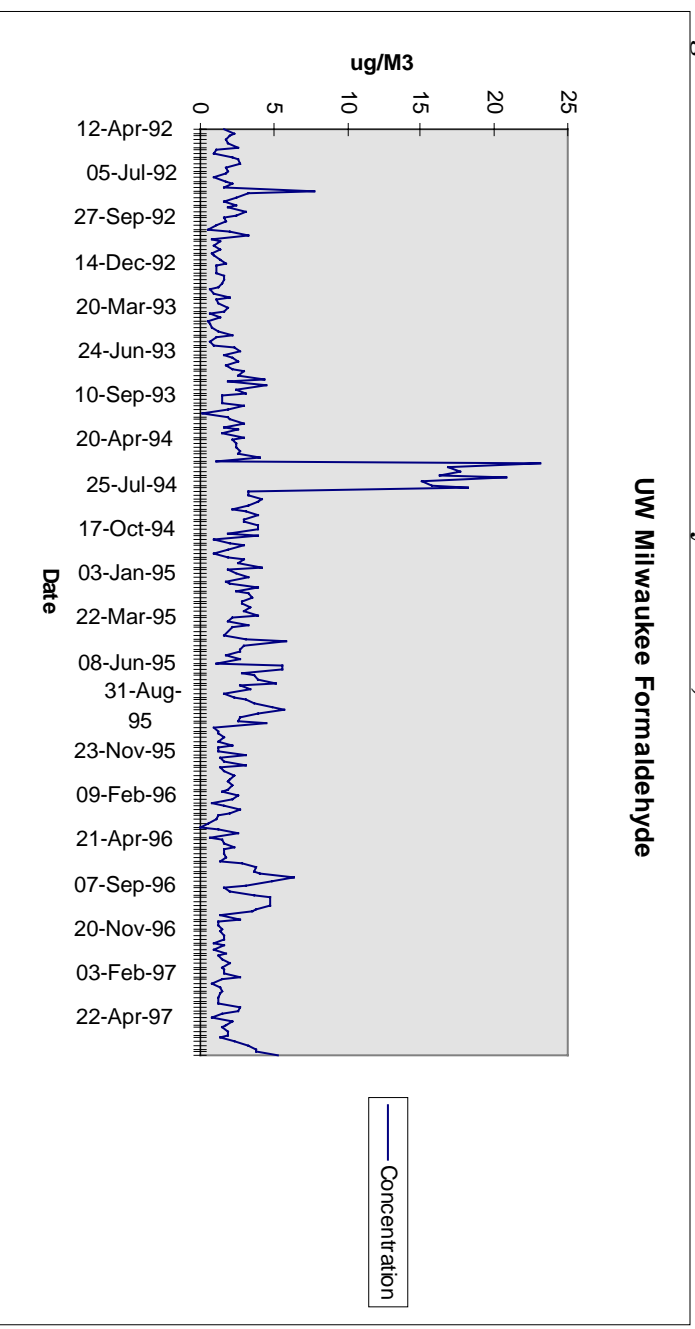


Figure 19: PAMS 24-Hour Formaldehyde Values, Values Below 10  $\mu\text{g}/\text{m}^3$   
UW Milwaukee Formaldehyde  
1994 High Values Excluded

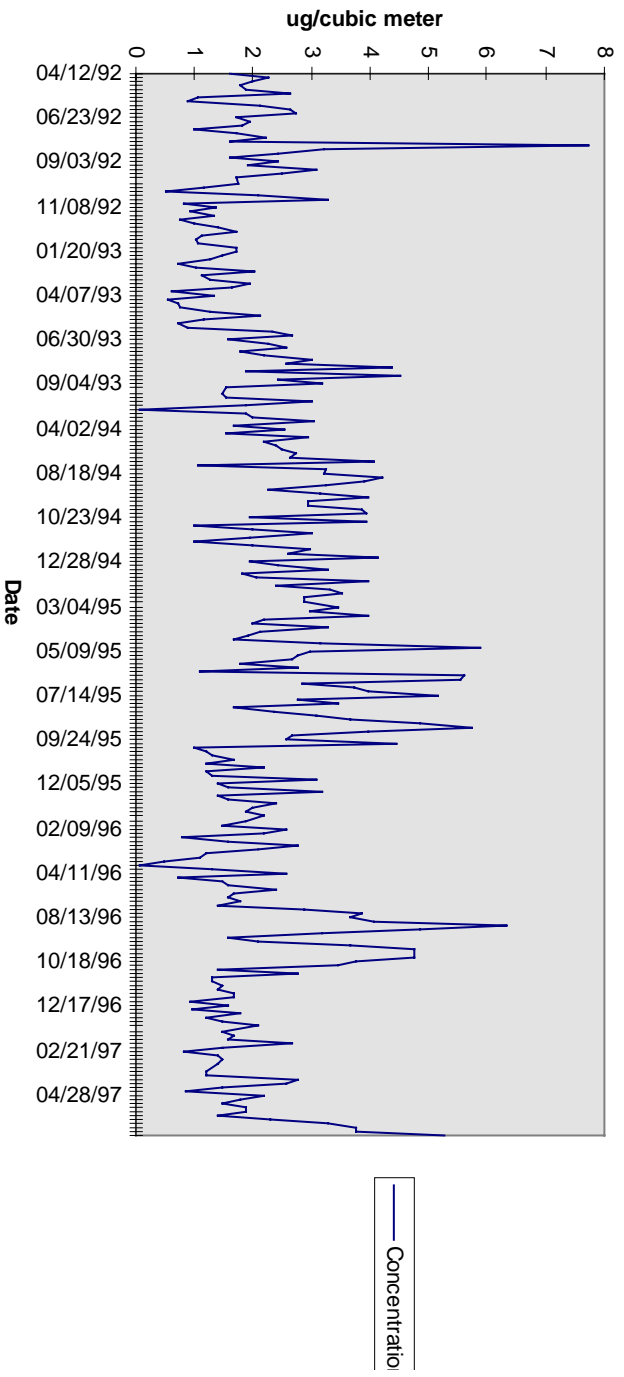


Figure 20: Comparison of Formaldehyde Results <10  $\mu\text{g}/\text{m}^3$

Milwaukee and Green Bay Formaldehyde

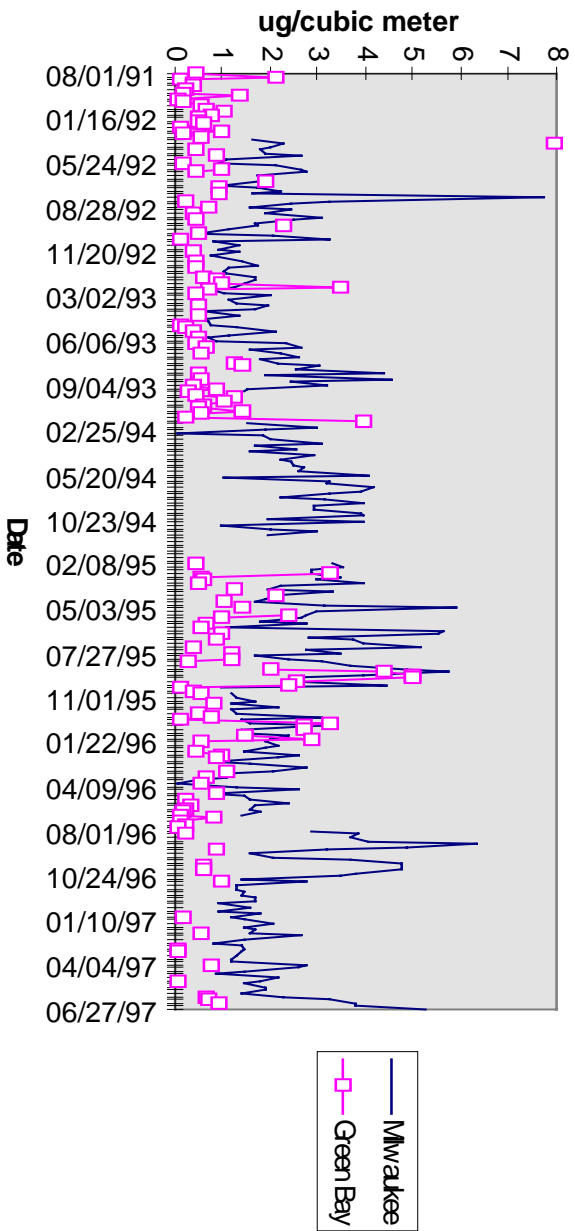
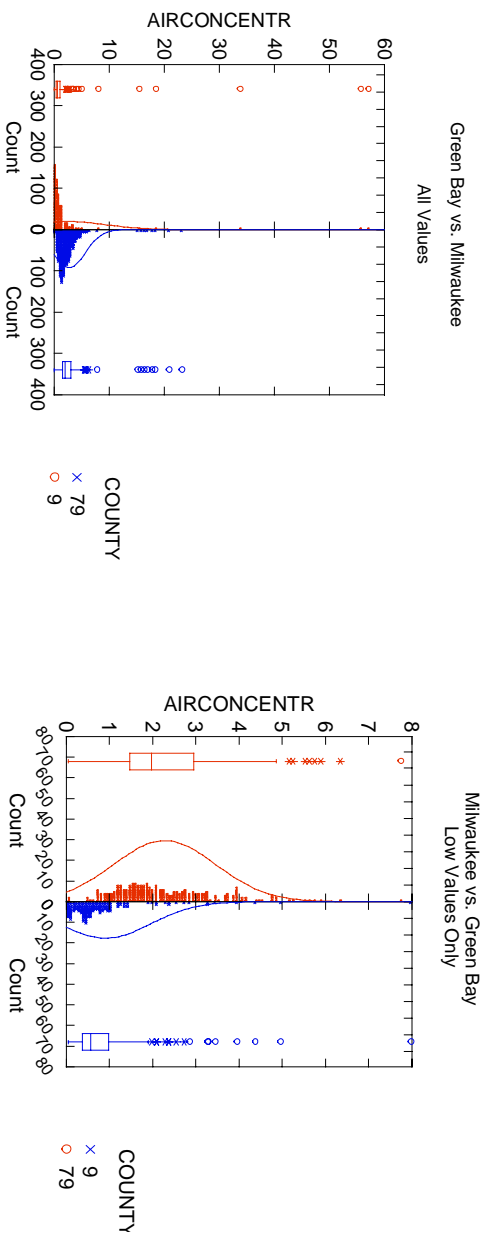


Figure 21: Results Distributions from Green Bay and Milwaukee



## Data Comparisons, Milwaukee Values

The Milwaukee data set was collected entirely at a single site, so that no inter-site comparison is necessary. Application of ANOVA to both the complete and truncated data sets yields statistically significant differences in both the yearly and seasonal variations. Significant values obtained from the statistical analyses are included in the tables below. It should be noted that the years determined to be statistically different have ranges that overlap each other considerably. It is probable that the statistical significance does not translate into a true trend or environmental difference between years, but rather represents a distribution of sampling events across the different years.

**Table 46: Significant Values from Yearly Statistical Analysis**

<b>Yearly</b>	<b>F-ratio =</b>	6.549	<b>P =</b>	0.000
<b>All Values</b>	<b>93</b>	<b>96</b>	<b>97</b>	
<b>94</b>	0.006			
<b>95</b>	0.000	0.003	0.011	
<b>Low Values</b>	<b>F-ratio =</b>	7.546	<b>P =</b>	0.000
<b>93</b>			0.012	
<b>95</b>	0.000	0.009		

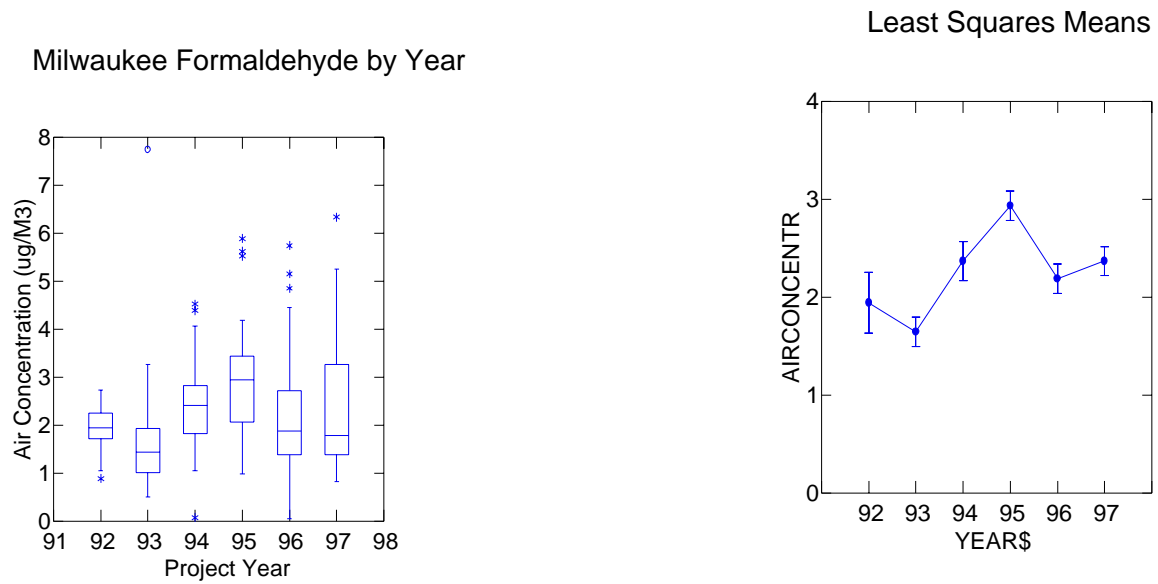
Results were separated by season, with 3-month periods beginning in December (winter) being associated with each season. ANOVA testing of the data grouped in this manner yields highly significant differences between summer and all other seasons ( $F = 17.066$  (full);  $21.903$  (short)  $\text{prob} = 0.000$ ). Table 47 summarizes the least square means and results to help investigate whether this statistical difference represents a potentially valid trend. Note that the questionable high values occurred only during the summer. The Box plots below present the yearly and seasonal data, showing the significant overlap in range that diminishes confidence in the statistical analysis.

**Table 47: Milwaukee Seasonal Statistical Values**

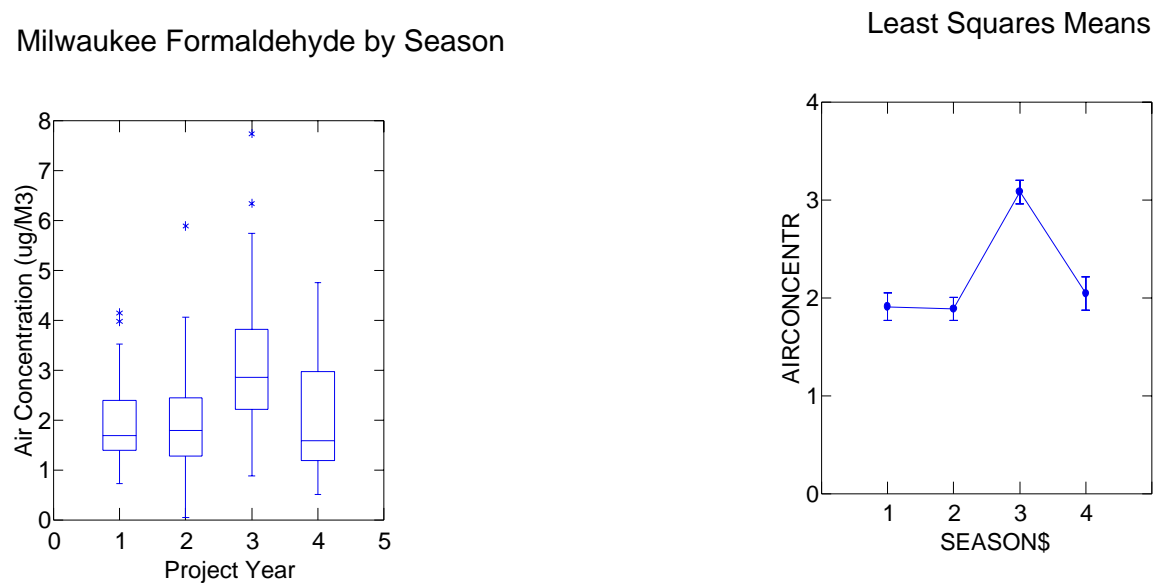
	<b>Winter</b>	<b>Spring</b>	<b>Summer, All</b>	<b>Summer, Low</b>	<b>Fall</b>
<b>Mean</b>	1.91	1.89	4.44	3.08	2.04
<b>Standard Error</b>	0.10	0.10	0.49	0.15	0.18
<b>Median</b>	1.70	1.79	3.07	2.85	1.59
<b>Standard Deviation</b>	0.79	0.93	4.55	1.31	1.16
<b>Relative Standard Dev (%)</b>	41.6%	49.1%	102.6%	42.4%	57.1%
<b>Range</b>	3.42	5.84	22.26	6.85	4.25
<b>Minimum</b>	0.73	0.05	0.89	0.89	0.51
<b>Maximum</b>	4.15	5.89	23.15	7.74	4.76
<b>Count</b>	60.00	84	88	80	40
<b>Confidence Level(95.0%)</b>	0.21	0.20	0.96	0.29	0.37



**Figure 22: Milwaukee Data Yearly Analysis**



**Figure 23: Seasonal Analysis**



## ***Formaldehyde Conclusions***

Analysis of the 24-hour Green Bay and Milwaukee formaldehyde sampling and analysis programs yields the following pertinent points of interest:

1. Milwaukee values tend to be slightly higher than values observed from the same time period at Green Bay. Median observed values are about 2.0 and 0.6  $\mu\text{g}/\text{m}^3$ , respectively.
2. Most values are less than 10  $\mu\text{g}/\text{m}^3$ , although a small number of values from each site exceed this value significantly.
3. No difference between the Bay Beach and Fox River sites could be discerned statistically. No yearly or seasonal differences are observable within the Green Bay data.
4. Both yearly and seasonal statistical differences are present in the Milwaukee data. A clear increasing or decreasing trend is not present with the yearly data, but summers appear consistently higher than the other seasons. Qualitative evaluation of the data shows a significant overlap between years and seasons that cast doubt upon whether the statistical differences represent valid trends within the data, although the observed summer trend could readily be indicative of increased heat and light related formaldehyde production occurring.

## Volatile Organic Compounds

### Overview

This broad designation includes a wide variety of compounds, including those in use as solvents, degreasers, gasoline components and products of incomplete combustion. The parameters incorporated into this study are part of a standard suite developed for EPA method TO-14. Most of them are chlorinated solvents, or products of incomplete combustion. Although this parameter list incorporates but a small fraction of potential VOC air contaminants, it includes many of the more potentially hazardous anthropogenic compounds of this class.

VOC testing has been a part of the WUATM program since it's inception in 1991. The original method employed adsorbent tube sampling, followed by thermal desorption and gas chromatographic analysis. This method was more technically challenging, in addition to yielding results that were difficult to interpret, and was superseded by whole air sampling in passivated stainless steel canisters in 1994. Sampling for the toxic VOC parameters in Milwaukee began in January 1997. In addition to the current data, an analysis of Green Bay results between 1994 and 1997 is included in this report for project closure.

### VOC Data Completeness

Project completeness with reference to VOCs is documented in the following table. Sampling Completeness is the ratio of ambient samples collected to total Sampling days. Analytical Completeness in this table is the ratio of Samples to Samples Submitted. It should be noted that the Green Bay sampler had a high number of voids associated with the installation of a new sampler and associated start up problems. Most of the duplicate samples were attempts at obtaining co-located samples comparing the old and new samplers.

**Table 48: VOC Completeness, Green Bay**

<b>Sampling Completeness</b>	<b>Samples</b>	<b>Voids</b>	<b>Ambient</b>	<b>Duplicates</b>	<b>Sampling Days</b>
86.7%	43	11	26	11	30
<b>Analytical Completeness</b>	<b>Samples</b>	<b>Ambient</b>	<b>Duplicates</b>	<b>Samples Submitted</b>	
96.9%	31	25	6	32	

**Table 49: VOC Completeness, Milwaukee**

<b>Sampling Completeness</b>	<b>Samples</b>	<b>Voids</b>	<b>Ambient</b>	<b>Duplicates</b>	<b>Sampling Days</b>
100.0%	18	2	15	2	15
<b>Analytical Completeness</b>	<b>Samples</b>	<b>Ambient</b>	<b>Duplicates</b>	<b>Samples Submitted</b>	
93.8%	15	14	1	16	

## VOC Analytical Results

The tables following present a summation of Toxics VOC data. The first table lists all parameters which were not detected in Green Bay during the course of sampling in 1996 and 1997. A total of 20 parameters are included. The second table presents the Milwaukee undetected parameters. A total of 25 parameters were not detected in Milwaukee. Parameters detected in Green Bay (number of detects in parenthesis) but not in Milwaukee include 1,1,1-trichloroethane (15); 1,1,2,2-tetrachloroethane (6); carbon tetrachloride (15); cumene (1); methyl chloride (16); and tetrachloroethene (1). In addition, chlorobenzene was detected once in Milwaukee, but not in Green Bay.

**Table 50: Undetected Parameters in Green Bay**

1,1,2-TRICHLOROETHANE	c-1,3-DICHLOROPROPENE
1,1-DICHLOROETHANE	CHLOROBENZENE
1,2-DICHLOROBENZENE	CHLOROETHANE
1,2-DICHLOROETHANE	CHLOROPRENE
1,2-DICHLOROPROPANE	DIBROMOCHLOROMETHANE
1,3-DICHLOROBENZENE	STYRENE
1,4-DICHLOROBENZENE	t-1,2-DICHLOROETHENE
BROMODICHLOROMETHANE	t-1,3-DICHLOROPROPENE
BROMOFORM	TRICHLOROETHENE
BROMOMETHANE	VINYLCHLORIDE

**Table 51: Undetected Parameters in Milwaukee**

1,1,1-TRICHLOROETHANE	CARBON TETRACHLORIDE
1,1,2,2-TETRACHLOROETHANE	CHLOROETHANE
1,1,2-TRICHLOROETHANE	CHLOROPRENE
1,1-DICHLOROETHANE	CUMENE (i-PROPYLBENZENE)
1,2-DICHLOROBENZENE	DIBROMOCHLOROMETHANE
1,2-DICHLOROETHANE	METHYLCHLORIDE
1,2-DICHLOROPROPANE	STYRENE
1,3-DICHLOROBENZENE	t-1,2-DICHLOROETHENE
1,4-DICHLOROBENZENE	t-1,3-DICHLOROPROPENE
BROMODICHLOROMETHANE	TETRACHLOROETHENE
BROMOFORM	TRICHLOROETHENE
BROMOMETHANE	VINYLCHLORIDE
c-1,3-DICHLOROPROPENE	

The following two tables present results from those samples which were detected at least once during the year in Green Bay and Milwaukee, respectively. Evaluation criteria are average, maximum, and minimum reported values, along with percent relative standard deviation. Additional reporting criteria include the number of detects, and how many samples reported each particular parameter. Values are reported as ppbv.

**Table 52: Green Bay Toxics VOC Results (ppbv)**

Parameter	Average	Maximum	Minimum	%RSD	Detects	Samples	Detection Rate
BENZENE	0.35	0.67	0.18	29.7%	31	31	100.0%
TOLUENE	0.66	1.50	0.29	46.2%	31	31	100.0%
XYLENES (m & p)	0.25	0.53	0.10	44.9%	31	31	100.0%
ACETYLENE	1.34	3.00	0.75	37.3%	30	31	96.8%
ETHYLBENZENE	0.10	0.20	0.05	42.9%	29	31	93.5%
PROPENE	0.26	0.56	0.06	42.9%	29	31	93.5%
o-XYLENE	0.11	0.30	0.05	52.6%	28	31	90.3%
METHYLENE CHLORIDE	0.12	0.29	0.10	37.9%	19	31	61.3%
METHYLCHLORIDE	0.35	0.70	0.10	68.7%	16	31	51.6%
1,1,1-TRICHLOROETHANE	0.23	1.00	0.10	102.7%	15	31	48.4%
CARBON TETRACHLORIDE	0.10	0.10	0.10	0.0%	15	31	48.4%
CHLOROFORM	0.12	0.28	0.10	40.5%	11	31	35.5%
1,1,2,2-TETRACHLOROETHANE	0.16	1.10	0.10	138.1%	6	31	19.4%
n-OCTANE	0.08	0.20	0.05	73.1%	5	31	16.1%
1,3 BUTADIENE	0.10				1	31	3.2%
CUMENE (i-PROPYLBENZENE)	0.06				1	31	3.2%
TETRACHLOROETHENE	0.10				1	31	3.2%

**Table 53: Milwaukee Toxics VOC Results (ppbv)**

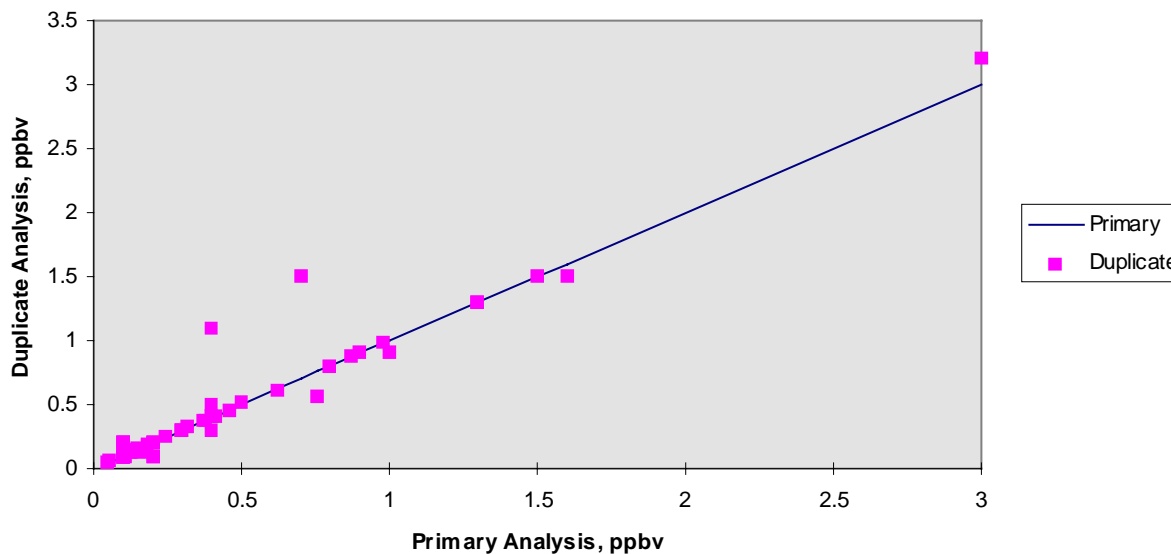
Parameter	Average	Maximum	Minimum	%RSD	Detects	Samples	Detection Rate
ACETYLENE	1.88	5.20	0.57	66.1%	15	15	100.0%
BENZENE	0.37	0.88	0.14	58.3%	15	15	100.0%
PROPENE	0.42	1.10	0.15	65.8%	15	15	100.0%
TOLUENE	0.64	1.40	0.18	55.5%	15	15	100.0%
METHYLENE CHLORIDE	0.24	0.68	0.10	70.9%	14	15	93.3%
XYLENES (m & p)	0.32	0.90	0.10	75.3%	12	15	80.0%
ETHYLBENZENE	0.10	0.25	0.05	59.0%	10	15	66.7%
o-XYLENE	0.12	0.32	0.05	68.9%	8	15	53.3%
1,3 BUTADIENE	0.11	0.21	0.10	26.2%	4	15	26.7%
n-OCTANE	0.05	0.10	0.05	22.5%	4	15	26.7%
CHLOROBENZENE	0.05	0.07	0.05	9.6%	1	15	6.7%
CHLOROFORM	0.12	0.35	0.10	55.3%	1	15	6.7%

## VOC Quality Assurance Parameters

The primary quality control samples collected during 1996 and 1997 were duplicate and co-located samples. Green Bay and Milwaukee samples in this category are considered together. A total of 6 duplicate samples were collected in Green Bay, while 1 was collected in Milwaukee. The graph below shows a comparison of duplicate samples analyzed for toxics parameters.

A total of 142 data pairs are represented in this table, with 57 detect pairs (40.1%), and 2 unacceptable pairs (1.8%). Non-detect pairs show qualitative agreement and are not incorporated into the graph. The average percent difference between the detect pairs is 14.5%. There are 11 detect pairs (7.7%) which fail the quality control limit of  $\pm 25\%$ . However, all but 3 (2.1%) of these differ by 0.1 ppbv or less.

**Figure 25: VOC Duplicates**



Analysis of field blanks has not been incorporated directly into the WUATM VOC sampling scheme. Part of the analysis contract specifies that canisters be cleaned to  $<10$  ppbc total, with individual target compounds present only at less than 0.1 ppb.

### **Historic VOC Data and Comparisons**

Comparisons of the data between different years and sites are complicated by several factors. The first is the change from adsorbent tube to canister sampling in 1994. There simply is no good way to compare the results obtained with these different techniques with confidence, so this report concentrates on the canister sampling results. A review of the adsorbent tube sampling results is available in the first Urban Air Toxics Monitoring report, DNR publication number AM-218-97.

The next complicating factor is a change in laboratory that occurred in January 1997. Prior to that time, analysis was conducted at Biospheric Research Corporation (BRC) in Hillsboro, Oregon, while the Wisconsin State Lab of Hygiene (SLOH) has conducted the analysis since. Although the same method is in place at each, there is some variation between detection limits and analytical interferences. Future trend analysis and inter-site comparisons should be possible, dating from the inception of analysis at SLOH.

For these reasons, no attempt has been made to conduct in-depth statistical analysis to determine whether there have been any observable trends with the VOC parameters. A qualitative examination of the data comparing the average and maximum concentrations of all parameters detected in Green Bay is summarized in the following table. It should be noted that blank entries in the "Average" column accompanied by an entry in the corresponding "Maxima" column indicates the parameter in question was detected only once. An entry of "ND" means that the parameter was not detected in that particular year. The years used refer to the project year, each of which ends in June of the year stated.

**Table 54: Yearly Green Bay Comparisons**

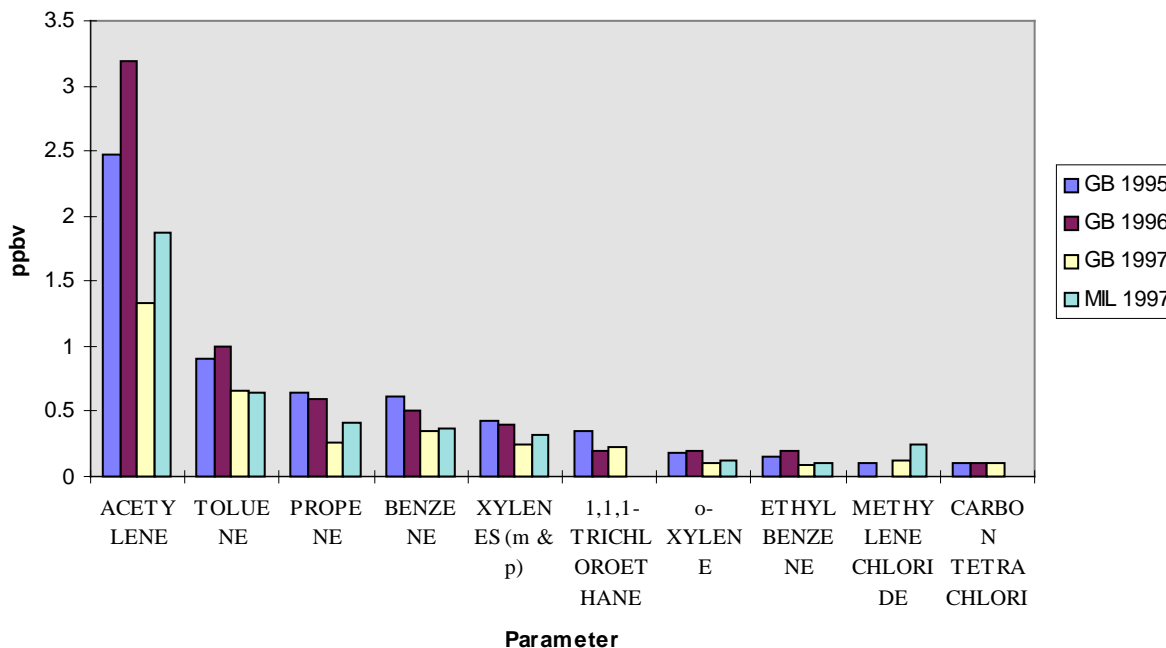
Parameter	AVERAGE			MAXIMA		
	1995	1996	1997	1995	1996	1997
ACETYLENE	2.5	3.2	1.3	4.7	7.3	3.0
TOLUENE	0.9	1.0	0.7	2.0	2.5	1.5
PROPENE	0.7	0.6	0.3	1.2	1.6	0.6
BENZENE	0.6	0.5	0.3	1.4	1.3	0.7
XYLENES (m & p)	0.4	0.4	0.2	0.8	1.3	0.5
1,1,1-TRICHLOROETHANE	0.4	0.2	0.2	0.7	0.4	1.0
o-XYLENE	0.2	0.2	0.1	0.3	0.5	0.3
ETHYLBENZENE	0.2	0.2	0.1	0.3	0.4	0.2
METHYLENE CHLORIDE	0.1	0.2	0.1	0.2	0.2	0.3
STYRENE	0.1	0.1	ND	0.4	0.2	ND
CARBON TETRACHLORIDE	0.1	0.1	0.1	0.1	0.1	0.1
METHYLCHLORIDE	0.1	0.2	<0.4	0.3	0.2	<0.7
n-OCTANE	0.1	0.1	0.1	0.1	0.1	0.2
TETRACHLOROETHENE	0.1	0.1		0.2	0.1	0.1
CHLOROFORM	0.1	0.1	0.1	0.1	0.7	0.3
BROMOMETHANE		ND	ND	0.2	ND	ND

CUMENE (I-PROPYLBENZENE)				0.2	0.1	0.1
TRICHLOROETHENE				0.2	0.1	ND
1,1,2,2-TETRACHLOROETHANE			0.2	0.1	0.2	1.1
1,4-DICHLOROBENZENE	ND		ND	ND	0.1	ND
1,3 BUTADIENE	ND	0.1		ND	0.2	0.1

It should be noted that the “<” values for 1997 Methylchloride results indicate analytical interference which limits the ability of the laboratory to report this parameter’s concentration in confidence.

A final comparison of the data is presented in the graph below. This graph illustrates the most frequently detected parameters for the 3 years of Green Bay data, and the single year of Milwaukee data. Both this and the table above indicate that there has not been a great deal of variation of these VOC parameters over the years.

**Figure 26: Most Detected Parameters**





## References

DNR Air Monitoring Handbook

Green Bay Urban Air Toxics Monitoring, A Summary Report for the Period July 1991 - June 1995, PUBL-AM-218-97, State of Wisconsin, Department of Natural Resources, 2/97 (GBUATM 95)

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